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JEE (Main & Advanced) & PMTs

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Contents

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Choosing Chemistry for a Profession

Chemistry as a main subject is very popular in colleges. In Bombay, chemical engineering is a very popular subject and is also highly competitive. This is because in a place like Bombay where textile manufacturing and many other engineering companies are in plenty, a good student of B.Tech can immediately get a job.

For research students, analysis is mostly instrumental. Instruments used for X-ray spectroscopy, diffraction, molecular and atomic spectroscopy, chromatography and γ-rays are available in any good institution and most of the instruments are also automatic. Biochemistry has recently picked up. But the reason for running away from maths will no longer hold good. Borrowed programs—either from institutions or the instrument manufacturers will only satisfy one's conscience that one is doing good work. Soon, one realises that you have to learn and write your own programs, and be brave enough to contradict the findings of big persons, if you have the confidence in your own work.

One does not select a topic for research because it is an easy topic. One should choose a topic because it is challenging. Read the life and work of the great scientists. This will inspire you to do big things in life. If you are a professor or teacher, tell stories about the scientists to the students, that will inspire them. Everyone who watches the Republic Day Parade and 'Beating of the Retreat' will wish that they had joined the army, navy or air force.

Science is the same. First get inspired and then work hard to achieve the target and then excel.

Anil Ahlawat
Editor

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CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.
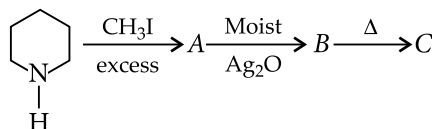
PROBLEM Set 20

JEE MAIN/PMTs

1. The nitrogen atoms in NH_3, NH_2^- and NH_4^+ are all surrounded by eight electrons. When these species are arranged in increasing order of HNH bond angle, correct order is
   (a) NH_3, NH_2^-, NH_4^+ (b) NH_4^+, NH_2^-, NH_3
   (c) NH_3, NH_4^+, NH_2^- (d) NH_2^-, NH_3, NH_4^+

2. Study the following data :
   $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$; $\Delta H° = -185$ kJ/mol
   $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$; $\Delta H° = -483.7$ kJ/mol

   Calculate ΔE at constant pressure and 25°C for the reaction given below :
   $$4HCl_{(g)} + O_{2(g)} \rightarrow 2Cl_{2(g)} + 2H_2O_{(g)}$$

   (a) – 111 kJ   (b) + 111 kJ
   (c) – 11.1 kJ   (d) + 11.1 kJ

3. In which of the following ionization processes, the bond order has increased and the magnetic behaviour has changed?
   (a) $N_2 \rightarrow N_2^+$ (b) $C_2 \rightarrow C_2^+$
   (c) $NO \rightarrow NO^+$ (d) $O_2 \rightarrow O_2^+$

4. Nitric oxide reacts with oxygen gas as
   $$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$

   Initially NO and O_2 are separated as shown in the diagram below. When the valve is opened the reaction quickly goes to completion. Identify the gases that remain at the end of the reaction and calculate their partial pressures. Assume temperature remains constant at 25°C.

   NO 4.00 L at 0.500 atm O_2 2.00 L at 1.00 atm
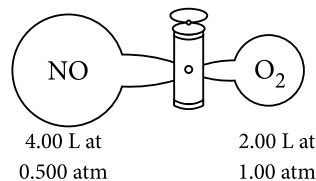
   (a) $p_{O_2} = 0.333$ atm; $p_{NO_2} = 0.167$ atm
   (b) $p_{NO} = 0.243$ atm; $p_{NO_2} = 0.133$ atm
   (c) $p_{O_2} = 0.133$ atm; $p_{NO} = 0.243$ atm
   (d) $p_{O_2} = 0.167$ atm; $p_{NO_2} = 0.333$ atm

5. Study the given reaction sequence and identify the most stable compound 'C'.

(a)   (b)

(c)   (d)

H_3C CH_3

6. 'A'(C_9H_8) decolourises Br_2 in CCl_4 and adds one equivalent of H_2 under mild conditions giving 'B'(C_9H_{10}). At high temperature and pressure, 'A' adds four equivalents of H_2 forming 'C'(C_9H_{16}). Vigorous oxidation of 'A', yields phthalic acid. The structures of 'A' and 'B' respectively are

(a)

(b)

(c)

(d)
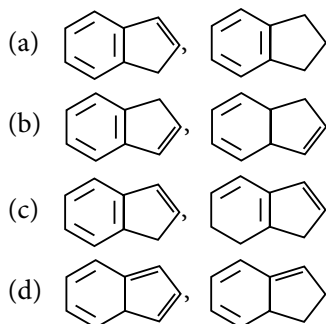
Halogens combine with each other to form interhalogen compounds (XX', XX'_3, XX'_5 and XX'_7). Halide ions often react with molecules of halogens or interhalogens to form polyhalide ions consisting either of the same halogen or of two or three different halogens. Besides these, a few other anions are known, which do not contain any of the halogen atoms but behave like halide ions. These anions are called pseudohalides and consist of two or more atoms of which one is always a nitrogen atom.

7. The isoelectronic pair is
   (a) Cl_2O, ICl_2^- (b) ICl_2^-, ClO_2
   (c) IF_2^+, I_3^- (d) ClO_2^-, ClF_2^+

8. The pseudohalide, polyhalide and interhalogen are respectively
   (a) BrI_2^-, OCN^-, IF_5 (b) IF_5, BrI_2^-, OCN^-
   (c) OCN^-, IF_5, BrI_2^- (d) OCN^-, BrI_2^-, IF_5

9. 50 mL of 1 M oxalic acid is shaken with 0.5 g wood charcoal. The final concentration of the solution after adsorption is 0.5 M. The amount of oxalic acid adsorbed per gram of carbon is

10. Total number of compounds that do not undergo Cannizzaro reaction is
    2-Methylpentanal, methanal, benzaldehyde, 1-phenylpropanone, phenylacetaldehyde, 2, 2-dimethylbutanal, benzophenone, cyclohexanone.

PRACTICE PAPER 2**Q**15

JEE Main

(Full Length)

PHYSICS

1. A square loop of side a is placed in the same plane as a long straight wire carrying a current I. The centre of the loop is at a distance r from the wire, where $r >> a$, as shown in figure. The loop is moved away from the wire with a constant velocity v. The induced emf in the loop is

   (a) $\dfrac{\mu_0 I a v}{2\pi r}$

   (b) $\dfrac{\mu_0 I a^3 v}{2\pi r^3}$

   (c) $\dfrac{\mu_0 I v}{2\pi}$
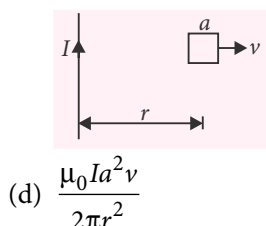
   (d) $\dfrac{\mu_0 I a^2 v}{2\pi r^2}$

2. An ideal massless spring S can be compressed 2 m by a force of 200 N. This spring is placed at the bottom of the frictionless inclined plane which makes an angle $\theta = 30°$ with the horizontal. A 20 kg mass is released from rest at the top of the inclined plane and is brought to rest momentarily after compressing the spring 4 m. Through what distance does the mass slide before coming to rest?

   (a) 2.2 m (b) 9.61 m

   (c) 8.16 m (d) 1.9 m

3. Two identical coherent sources placed on a diameter of a circle of radius R at separation $x (<< R)$ symmetrically about the centre of the circle. The sources emit identical wavelength λ each. The number of points on the circle with maximum intensity is $(x = 5\lambda)$.

   (a) 24 (b) 20

   (c) 22 (d) 26

4. The ratio of the concentration of electrons and of holes in a semiconductor is $\dfrac{7}{5}$ and the ratio of currents is $\dfrac{7}{4}$, then what is the ratio of their drift velocities?

   (a) $\dfrac{4}{7}$ (b) $\dfrac{5}{8}$

   (c) $\dfrac{4}{5}$ (d) $\dfrac{5}{4}$

5. A progressive wave moving along x-axis is represented by

   $$y = A\sin\left[\dfrac{2\pi}{\lambda}(vt - x)\right]$$

   The wavelength (λ) at which the maximum particle velocity is 3 times the wave velocity is

   (a) $\dfrac{A}{3}$ (b) $\dfrac{2A}{(3\pi)}$

   (c) $\left(\dfrac{3}{4}\right)\pi A$ (d) $\left(\dfrac{2}{3}\right)\pi A$

6. A positive charged thin metal ring of radius R is fixed in the x-y plane with the centre at the origin O. A negatively charged particle P is released from rest at the point $(0, 0, z_0)$, where $z_0 > 0$. Then, the motion of P is

   (a) periodic, for all values of z_0 satisfying $0 < z_0 < \infty$.

   (b) simple harmonic, for all values of z_0 satisfying $0 \le < z_0 \le R$.

   (c) approximately simple harmonic, provided $z_0 << R$.

   (d) such that P crosses O and continues to move along the negative z-axis towards $x = -\infty$.
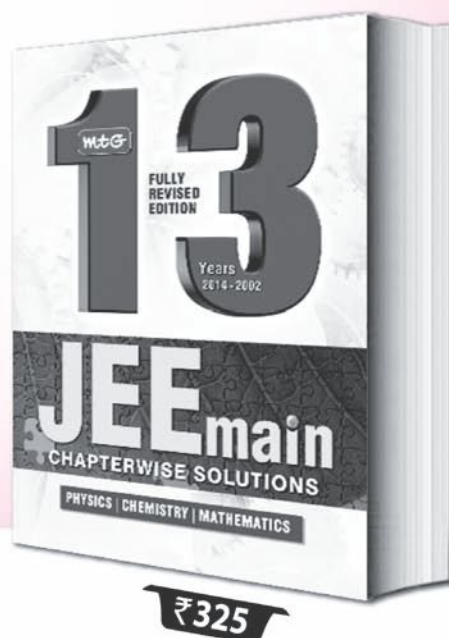
7. The length of a potentiometer wire is l. A cell of emf ε is balanced at a length $l/5$ from the positive end of the wire is. If length of the wire is increased by $l/2$. At what distance will the same cell give a balance point.

(a) $\frac{2}{15}l$ (b) $\frac{3}{15}l$

(c) $\frac{3}{10}l$ (d) $\frac{4}{10}l$

8. A block of mass 1 kg is placed over a plank of mass 2 kg. The length of the plank is 2 m. Coefficient of friction between the block and the plank is 0.5 and the ground over which the plank is placed is smooth. A constant force $F = 30$ N is applied on the plank in horizontal direction. The time after which the block will separate from the plank is (Take $g = 10$ m s^{-2})

(a) 0.73 s   (b) 1.2 s

(c) 0.62 s   (d) 1.6 s

9. A light rod of length 200 cm is suspended from the ceiling horizontally by means of two vertical wires of equal length tied to its ends. One of wires is made of steel and is of cross-section 0.1 cm^2 and the other of brass of cross-section 0.2 cm^2. Along the rod at which distance a weight may be hung to produce equal stresses in both the wires?

(a) $\frac{4}{3}$ m from steel wire

(b) $\frac{4}{3}$ m from brass wire

(c) 1 m from steel wire

(d) $\frac{1}{4}$ m from brass wire

10. Diameter of a plano-convex lens is 6 cm and thickness at the centre is 3 mm. If the speed of light in the material of the lens is 2×10^8 m s^{-1}, the focal length of the lens is

(a) 15 cm   (b) 20 cm

(c) 30 cm   (d) 10 cm

11. A horizontal rod rotates about a vertical axis through one end. A ring, which can slide along the rod without friction, is initially close to the axis and then slides to the other end of the rod. In this process, which of the following quantities will be conserved? [L = angular momentum, K_T = total kinetic energy, K_R = rotational kinetic energy]

(a) L only   (b) L and K_T only

(c) L and K_R only   (d) K_T only

12. A vessel whose bottom has round hole with diameter of 1 mm is filled with water. Only surface tension acts at hole. (Surface tension of water is 75×10^{-3} N m^{-1} and $g = 10$ m s^{-2}). The maximum height (in cm) to which water can be filled in the vessel without leakage is

(a) 2   (b) 3

(c) 4   (d) 1

13. The incident intensity on a horizontal surface at sea level from sun is about 1 kW m^{-2}. Assuming that 50 percent of this intensity is reflected and 50 percent is absorbed, the radiation pressure on this horizontal surface is

(a) 5×10^{-11} Pa   (b) 5×10^{-6} Pa

(c) 1×10^{-6} Pa   (d) 1×10^{-11} Pa

14. A electron of mass m_e initially at rest moves through a certain distance in a uniform electric field in time t_1. A proton of mass m_p also initially at rest takes time t_2 to move through an equal distance in this uniform electric field. Neglecting the effect of gravity, the ratio $\frac{t_2}{t_1}$ is nearly equal to

(a) $\left(\dfrac{m_e}{m_p}\right)^{1/2}$ (b) $\left(\dfrac{m_p}{m_e}\right)^{1/2}$

(c) 1   (d) 1836

15. A wide rectangular vessel has two holes on the vertical sides on opposite sides. Each hole has a cross-sectional area S. The height difference between them is Δh. What is the resultant force of reaction of the water flowing from the vessel?

(a) $F = \dfrac{\Delta h g \rho S}{2}$ (b) $F = \dfrac{\Delta h g \rho S}{4}$

(c) $F = \Delta h g \rho S$ (d) $F = 2\Delta h g \rho S$

16. An object of mass 0.2 kg executes simple harmonic oscillations along the x-axis with a frequency $\dfrac{25}{\pi}$ Hz. At the position $x = 0.04$ m, the object has kinetic energy 0.5 J and potential energy 0.4 J. The amplitude of oscillation is (Potential energy is zero at mean position)
(a) 6 cm   (b) 4 cm
(c) 8 cm   (d) 2 cm

17. Given that a photon of light of wavelength 10,000 Å has an energy equal to 1.23 eV. When light of wavelength 5000 Å and intensity I_0 falls on a photoelectric cell, the surface current is 0.40×10^{-6} A and the stopping potential is 1.36 V, then the work function is
(a) 0.43 eV   (b) 0.55 eV
(c) 1.10 eV   (d) 1.53 eV

18. Three metal rods of the same material and identical in all respects are joined as shown in the figure. The temperatures at the ends are maintained as indicated. Assuming no loss of heat from the curved surfaces of the rods, the temperature at the junction X would be
(a) 45°C
(b) 60°C
(c) 30°C
(d) 20°C
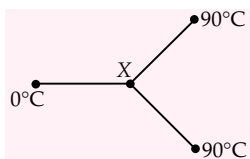
19. Velocity of sound in an open organ pipe is 330 m s^{-1}. The frequency of wave is 1.1 kHz and the length of tube is 30 cm. To which harmonic does this frequency correspond?
(a) 2$^{\text{nd}}$ (b) 3$^{\text{rd}}$
(c) 4$^{\text{th}}$ (d) 5$^{\text{th}}$

20. The following configuration of gates is equivalent to
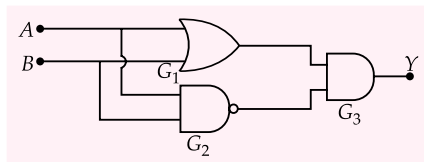
(a) NAND   (b) XOR
(c) OR   (d) AND

21. An inductance coil is connected to an ac source through a 60 Ω resistance in series. The source voltage, voltage across the coil and voltage across the resistance are found to be 33 V, 27 V and 12 V respectively. Therefore, the resistance of the coil is
(a) 30 Ω   (b) 45 Ω
(c) 105 Ω   (d) 75 Ω

22. If the work done in blowing a soap bubble of volume V is W, then the work done in blowing a soap bubble of volume 2 V will be
(a) W (b) 2 W
(c) $\sqrt{2}W$ (d) $W(4)^{1/3}$

23. Two polaroids are kept crossed to each other. Now one of them is rotated through an angle of 45°. The percentage of incident light now transmitted through the system is
(a) 15%   (b) 25%
(c) 50%   (d) 60%

24. A spherical conductor A of radius r is placed concenctrically inside a conducting shell B of radius $R(R > r)$. A charge Q is given to A, and then A is joined to B by a metal wire. The charge flowing from A to B will be
(a) $Q\left(\dfrac{R}{R+r}\right)$ (b) $Q\left(\dfrac{r}{R+r}\right)$
(c) Q (d) zero

25. Consider a two particle system with particles having masses m_1 and m_2. If the first particle is pushed towards the centre of mass through a distance d, by what distance should the second particle be moved, so as to keep the centre of mass at the same position?
(a) $\dfrac{m_2}{m_1}d$ (b) $\dfrac{m_1}{m_1+m_2}d$
(c) $\dfrac{m_1}{m_2}d$ (d) d

26. A radioactive source in the form of metal sphere of diameter 10^{-3} m emits beta particle at a constant rate of 6.25×10^{10} particles per second. If the source is electrically insulated, how long will it take for its potential to rise by 1 V, assuming that 80% of the emitted beta particles escape from the source?
(a) 6.95 µs   (b) 0.95 µs
(c) 1.95 µs   (d) 2.15 µs

27. The ratio of the rotational kinetic energy to the total kinetic energy of one mole of a gas of rigid diatomic molecules is

(a) $\dfrac{2}{3}$　　　　　(b) $\dfrac{2}{5}$

(c) $\dfrac{3}{5}$　　　　　(d) $\dfrac{5}{2}$

28. The largest wavelength in the ultraviolet region of the hydrogen spectrum is 122 nm. The smallest wavelength in the infrared region of the hydrogen spectrum (to the nearest integer) is

(a) 802 nm　　　　(b) 823 nm
(c) 1882 nm　　　(d) 1648 nm

29. A launching vehicle carrying an artificial satellite of mass m is set for launch on the surface of the earth of mass M and radius R. If the satellite is intended to move in a circular orbit of radius $7R$, the minimum energy required to be spent by the launching vehicle on the satellite is (Gravitational constant = G)

(a) $\dfrac{GMm}{R}$　　　　(b) $\dfrac{13GMm}{14R}$

(c) $\dfrac{GMm}{7R}$　　　　(d) $\dfrac{GMm}{14R}$

30. An ideal gas is taken through the cycle $A \to B \to C \to A$, as shown in the figure. If the net heat supplied to the gas in the cycle is 5 J, the work done by the gas in the process $C \to A$ is

(a) – 5 J　　　　　(b) –10 J
(c) –15 J　　　　　(d) –20 J
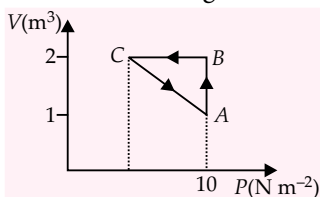
CHEMISTRY

31. Which of the following forms of interhalogen compounds does not exist?

(a) IF_7　　　　　(b) ClF_3
(c) ICl　　　　　(d) $BrCl_7$

32. Which pair of reagents would give the following amine by reductive amination?

$X + Y \xrightarrow{\text{H}_2/\text{Pd}}$
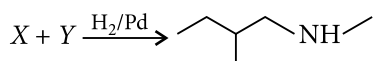
(a) Methylamine and 2-methylbutanoic acid
(b) NH_3 and 3-methyl-2-pentanone
(c) Methylamine and 2-methylbutanal
(d) Dimethylamine and 2-butanone

33. The gold number of gelatin, haemoglobin and sodium acetate are 0.005, 0.05 and 0.7 respectively. The protective actions will be in the order of

(a) gelatin < haemoglobin < sodium acetate
(b) gelatin > haemoglobin > sodium acetate
(c) haemoglobin > gelatin > sodium acetate
(d) sodium acetate > gelatin > haemoglobin.

34. The ionic mobility of alkali metal ions in aqueous solution is maximum for

(a) K^+　　　　　(b) Rb^+
(c) Li^+　　　　　(d) Na^+

35. Consider the following pair of compounds:
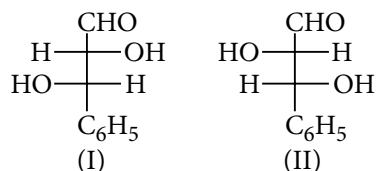
Which of the following statements is correct?
1. Both are enantiomers.
2. Both are in threo form.
3. Both are diastereomers.
4. Both are in erythro form.

(a) 1 and 2　　　　(b) 1, 2 and 3
(c) 2 and 3　　　　(d) 3 and 4

36. How many unit cells are present in a cube shaped ideal crystal of NaCl of mass 1.00 g? [Atomic mass : Na = 23, Cl = 35.5]

(a) 2.57×10^{21}　　(b) 5.14×10^{21}
(c) 1.28×10^{21}　　(d) 1.71×10^{21}

37. If M is element of actinoids series, the degree of complex formation decreases in the order

(a) $M^{4+} > M^{3+} > MO_2^{2+} > MO_2^+$
(b) $MO_2^+ > MO_2^{2+} > M^{3+} > M^{4+}$
(c) $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$
(d) $MO_2^{2+} > MO_2^+ > M^{4+} > M^{3+}$

38. Benzaldehyde undergoes Claisen condensation with another aldehyde to give cinnamaldehyde. The aldehyde is

(a) formaldehyde   (b) acetaldehyde
(c) crotonaldehyde   (d) propanaldehyde.

39. A mixture of $CaCl_2$ and NaCl weighing 4.44 g is treated with sodium carbonate solution to precipitate all the Ca^{2+} ions as calcium carbonate. The calcium carbonate so obtained is heated strongly to get 0.56 g of CaO. The percentage of NaCl in the mixture (atomic mass of Ca = 40) is
(a) 75   (b) 30.6
(c) 25   (d) 69.4

40. Copper carbonate and copper hydroxide both are present in
1.   Malachite   2.   Azurite
3.   Chalcocite   4.   Verdigris
(a) 1, 2, 3   (b) 1, 2
(c) 2, 4   (d) 2, 3, 4

41. Identify the product Z in the given sequence of reactions:

$$CH_3CN \xrightarrow{Na/C_2H_5OH} X \xrightarrow{HNO_2} Y \xrightarrow[\text{reagent}]{\text{Baeyer's}} Z$$
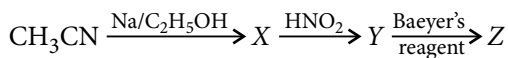
(a) CH_3CHO (b) CH_3CONH_2
(c) CH_3COOH (d) CH_3CH_2NHOH

42. Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2}$ = 3.00 hours. What fraction of sample of sucrose remains after 8 hours?
(a) 2.586   (b) 0.158
(c) 8.058   (d) 3.084

43. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of
(a) nitrogen   (b) oxygen
(c) carbon dioxide   (d) argon.

44. A mixture of camphor and benzoic acid can be easily separated by
(a) sublimation
(b) extraction with solvent
(c) fractional crystallisation
(d) chemical method.

45. By how many folds the temperature of a gas would increase when the root mean square velocity of the gas molecules in a container of fixed volume is increased by 5×10^4 cm/s to 10×10^4 cm/s?
(a) Two   (b) Three
(c) Six   (d) Four
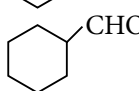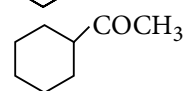
46. SO_2 and NO_2 cause pollution by increasing
(a) alkalinity   (b) neutrality
(c) acidity   (d) buffer action.

47. Identify the product 'C' in the given sequence of reactions:
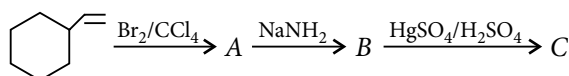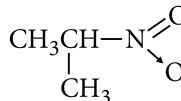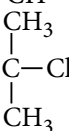
48. If an endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point, then
(a) ΔH is –ve, ΔS is +ve
(b) ΔH and ΔS both are +ve
(c) ΔH and ΔS both are –ve
(d) ΔH is +ve, ΔS is –ve.

49. Which of the following is not a nitro-derivative?

50. Which is least reactive towards nucleophilic substitution (S_N2)?
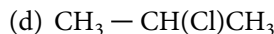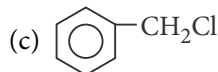
51. Consider the cell,
$Ag|AgBr_{(s)}, Br^-||AgCl_{(s)}, Cl^-|Ag$ at 25°C. The solubility products of AgCl and AgBr are 1×10^{-10} and 5×10^{-13} respectively. For what ratio of the concentrations of Br^- and Cl^- ions would the EMF of the cell be zero?
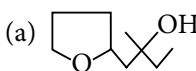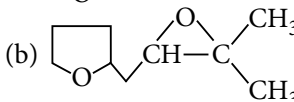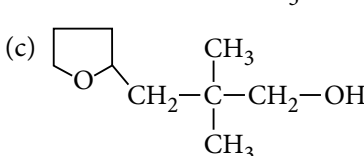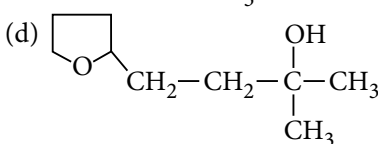
(a) $\dfrac{200}{1}$ (b) $\dfrac{1}{160}$

(c) $\dfrac{1}{200}$ (d) $\dfrac{160}{1}$

52. Which of the following is not a synthetic polymer?
(a) Polyethylene   (b) PVC
(c) Nylon   (d) Cellophane

53.
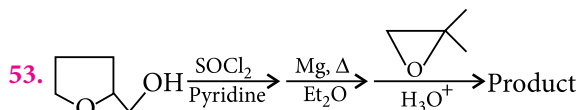
Product of the above reaction is

(a)

(b)

(c)

(d)

54. The equilibrium constant for the reaction,
$$SO_{2(g)} + NO_{2(g)} \rightleftharpoons SO_{3(g)} + NO_{(g)}$$
has a numerical value of 3.00 at a given temperature. 1.50 mol each of SO_2 and NO_2 are mixed in a 1.00 L flask and allowed to reach equilibrium. What percent of SO_2 is converted into product?
(a) 62.9%   (b) 60.3%
(c) 63.4%   (d) 59.4%
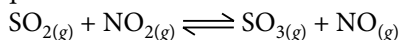
55. One mole of the complex compound $Co(NH_3)_5Cl_3$, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of $AgNO_3$ solution to yield two moles of $AgCl(s)$. The structure of the complex is
(a) $[Co(NH_3)_5Cl]Cl_2$
(b) $[Co(NH_3)_3Cl_3] \cdot 2NH_3$
(c) $[Co(NH_3)_4Cl_2]Cl \cdot NH_3$
(d) None of these

56. For which of the following amino acid, Van Slyke estimation method is not applicable?
(a) Alanine   (b) Aspartic acid
(c) Serine   (d) Proline
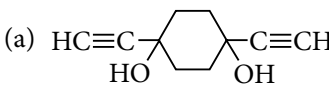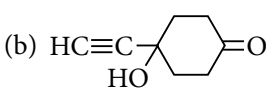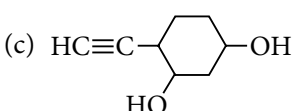
57. The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of which of the following are mixed?
(a) 10^{-4} M $Ca^{2+} + 10^{-4}$ M F^-
(b) 10^{-2} M $Ca^{2+} + 10^{-3}$ MF^-
(c) 10^{-5} M $Ca^{2+} + 10^{-3}$ M F^-
(d) 10^{-3} M $Ca^{2+} + 10^{-5}$ MF^-

58. Which of the following halides is least stable and has doubtful existence?
(a) CI_4 (b) GeI_4
(c) SnI_4 (d) PbI_4

59. The product of the reaction of cyclohexa-1,4-dione with acetylene in acidic medium is

(a)

(b)

(c)

(d) no reaction

60. The freezing point of equimolal aqueous solution will be highest for
(a) glucose   (b) $La(NO_3)_2$
(c) $Ca(NO_3)_2$ (d) $C_6H_5NH_3Cl$

MATHEMATICS

61. Let $[x]$ and $\{x\}$ denote the intergral part and fractional part of x, respectively. Then the number of solutions of the equation $4\{x\} = x + [x]$ is
(a) 1   (b) 2
(c) 0   (d) infinite

62. The range of the function f defined by
$$f(x) = \frac{e^x - e^{|x|}}{e^x + e^{|x|}} \text{ is}$$
(a) $[0, 1]$ (b) $(-1, 0]$
(c) $(0, 1)$ (d) $[-1, 0]$

63. If z is a complex number and $i = \sqrt{-1}$, then the minimum possible value of $|z|^2 + |z - 3|^2 + |z - 6i|^2$ is
(a) 15   (b) 30
(c) 20   (d) 45

64. Let α be a root of $ax^2 + bx + c = 0$ and β be a root of $ax^2 - bx - c = 0$, where a, b and c are real numbers and $a \neq 0$. Then the equation $\dfrac{a}{2}x^2 + bx + c = 0$ has a root γ such that
(a) $\gamma < \min\{\alpha, \beta\}$
(b) $\gamma > \max\{\alpha, \beta\}$
(c) γ lies between α and β
(d) $-\gamma$ lies between α and β

65. The maximum value of $\cos \alpha_1 \cdot \cos \alpha_2 \cdot \cos \alpha_3 \ldots \cos \alpha_n$ under the restriction $0 \leq \alpha_1, \alpha_2, \ldots, \alpha_n \leq \dfrac{\pi}{2}$ and $\cot \alpha_1 \cdot \cot \alpha_2 \ldots \cot \alpha_n = 1$ is
(a) $\dfrac{1}{2^{n/2}}$ (b) $\dfrac{1}{2^n}$
(c) $\dfrac{-1}{2^n}$ (d) 1

66. The general solution of the equation $(\sqrt{3} - 1)\sin\theta + (\sqrt{3} + 1)\cos\theta = 2$ is
(a) $n\pi + (-1)^n \dfrac{\pi}{4} - \dfrac{\pi}{12}$ (b) $2n\pi \pm \dfrac{\pi}{4} - \dfrac{\pi}{12}$
(c) $n\pi + (-1)^n \dfrac{\pi}{4} + \dfrac{\pi}{12}$ (d) $2n\pi \pm \dfrac{\pi}{4} + \dfrac{\pi}{12}$

67. A line through $A(-5, -4)$ meets the lines $x + 3y + 2 = 0$, $2x + y + 4 = 0$ and $x - y - 5 = 0$ at B, C and D respectively.
If $\left(\dfrac{15}{AB}\right)^2 + \left(\dfrac{10}{AC}\right)^2 = \left(\dfrac{6}{AD}\right)^2$, then the equation of the line is
(a) $2x + 3y + 22 = 0$ (b) $5x - 4y + 7 = 0$
(c) $3x - 2y + 3 = 0$ (d) none of these

68. If length of the intercept on the axes are 6 and 15 respectively and length of the tangent drawn from origin to the circle is of 4 units, then equation of the circle if its centre lie in the first quadrant, is
(a) $x^2 + y^2 - 10x - 17y + 16 = 0$
(b) $x^2 + y^2 - 17x - 10y + 16 = 0$
(c) $x^2 + y^2 + 8x + 19y + 18 = 0$
(d) none of these

69. Let P be a variable point on the ellipse $\dfrac{x^2}{25} + \dfrac{y^2}{16} = 1$ with foci at S and S'. If A be the area of triangle PSS', then the maximum value of A is
(a) 24 sq. units   (b) 20 sq. units
(c) 36 sq. units   (d) none of these

70. $3\tan^{-1}\left(\dfrac{1}{2}\right) + 2\tan^{-1}\left(\dfrac{1}{5}\right) + \sin^{-1}\left(\dfrac{142}{65\sqrt{5}}\right)$ is equal to
(a) $\dfrac{\pi}{2}$ (b) π
(c) $\dfrac{3\pi}{4}$ (d) $-\pi$

71. If the scalar product of the vector $\hat{i} + \hat{j} + \hat{k}$ with the unit vector in the direction of the resultant of the vectors $2\hat{i} + 4\hat{j} - 5\hat{k}$ and $\lambda\hat{i} + 2\hat{j} + 3\hat{k}$ is unity, then λ equals
(a) 5   (b) 2
(c) 1   (d) -1

72. The probability of the birth dates of all 6 persons to fall in only two different months is
(a) $\dfrac{341}{12^6}$ (b) $\dfrac{341}{12^5}$
(c) $\dfrac{341}{12^4}$ (d) $\dfrac{541}{12^6}$

73. If a, b, c are the sides of a triangle, then $\dfrac{a^2 + b^2 + c^2}{ab + bc + ca}$ is
(a) ≥ 1 (b) < 2
(c) Both (a) and (b)   (d) None of these

74. If $f(x) = \dfrac{1}{1 - x}$, then the points of discontinuity of the function $f[f\{f(x)\}]$ are
(a) $\{0\}$ (b) $\{0, 1\}$
(c) $\{1, -1\}$ (d) none of these

75. If $l_1 = \lim\limits_{x \to 2^+}(x + [x])$, $l_2 = \lim\limits_{x \to 2^-}(2x - [x])$ and $l_3 = \lim\limits_{x \to \pi/2}\dfrac{\cos x}{(x - \pi/2)}$, then
(a) $l_1 < l_2 < l_3$ (b) $l_2 < l_3 < l_1$
(c) $l_3 < l_2 < l_1$ (d) $l_1 < l_3 < l_2$

76. If the function $f(x) = 3 \cos |x| - 6ax + b$ increases for all $x \in R$, then the range of values of a is given by

(a) $a > -\dfrac{1}{2}$
(b) $a < -\dfrac{1}{2}$
(c) $a \le b$
(d) $a \ge b$

77. If in the expansion of $(1 + x)^m \cdot (1 - x)^n$, the coefficients of x and x^2 are 3 and –6, respectively, then m and n are respectively

(a) 12, 9
(b) 13, 9
(c) 9, 13
(d) 9, 12

78. If the product of the matrices
$$\begin{bmatrix} 1 & 1 \\ 0 & 1 \end{bmatrix}\begin{bmatrix} 1 & 2 \\ 0 & 1 \end{bmatrix}\begin{bmatrix} 1 & 3 \\ 0 & 1 \end{bmatrix}...\begin{bmatrix} 1 & n \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 378 \\ 0 & 1 \end{bmatrix}$$
then n is equal to

(a) 27
(b) 26
(c) 376
(d) 378

79. $\displaystyle\int_0^{\pi/2} \log\left(\dfrac{4 + 3\sin x}{4 + 3\cos x}\right) dx =$

(a) 0
(b) 1
(c) $\log 2$
(d) $\dfrac{\pi}{2}$

80. If $\cos\left(\dfrac{dy}{dx}\right) = a$, where $a \in R$, when $y = 2$ and $x = 0$, then

(a) $y = a \cos^{-1} x + 2$
(b) $y = x \cos^{-1} a + 2$
(c) $y = \dfrac{1}{\sqrt{1 - a^2}} + 2$
(d) none of these

81. A merchant plans to sell two types of personal computers, a desktop model and a portable model that will cost ₹ 25000 and ₹ 40000, respectively. He estimates that the total monthly demand of computers will not exceed 250 units. Determine the number of units of each type of computers which the merchant should stock to get maximum profit, if he does not want to invest more than ₹ 70 lakhs and his profit on the desktop model is ₹ 4500 and on the portable model is ₹ 5000.

(a) 180, 70
(b) 250, 0
(c) 200, 50
(d) 0, 175

82. The area of the region bounded by the parabolas $y^2 = 4ax$ and $x^2 = 4ay$ is

(a) $\dfrac{32a}{3}$ sq. units
(b) $\dfrac{32a^2}{3}$ sq. units
(c) $\dfrac{16a}{3}$ sq. units
(d) $\dfrac{16a^2}{3}$ sq. units

83. Find the equation of plane passing through the point $P(1, 1, 1)$ and containing the line $\vec{r} = (-3\hat{i} + \hat{j} + 5\hat{k}) + \lambda(3\hat{i} - \hat{j} - 5\hat{k})$.

(a) $x - 2y - z = 0$
(b) $x + 2y + z = 0$
(c) $x - 4y + 2z = 0$
(d) $x - 2y + z = 0$

84. The number of solutions of the equation
$$|x - 3|^{(x^2 - 8x + 15)/(x-2)} = 1 \text{ is}$$

(a) 1
(b) 2
(c) 0
(d) 4

85. If $x = \cos\alpha + i\sin\alpha$ and $y = \cos\beta + i\sin\beta$, then $(x - y)/(x + y)$ is equal to

(a) $i\tan\left(\dfrac{\alpha - \beta}{2}\right)$
(b) $-i\tan\left(\dfrac{\alpha - \beta}{2}\right)$
(c) $i\tan\left(\dfrac{\alpha + \beta}{2}\right)$
(d) $-i\tan\left(\dfrac{\alpha + \beta}{2}\right)$

86. The variance of 20 observations is 5. If each observation is multiplied by 2, then the new variance of the resulting obsevations is

(a) $2^3 \times 5$
(b) $2^2 \times 5$
(c) 2×5
(d) $2^4 \times 5$

87. The negation of the statement
p : "for every positive real number x, the number $x - 1$ is also positive" is

(a) "there exists atleast one positive real number x for which $(x - 1)$ is not positive"
(b) "for every positive real number x, the number $(x + 1)$ is also positive"
(c) Both (a) and (b)
(d) None of these

88. For all $n \in N$,
$$\left(1 + \dfrac{3}{1}\right)\left(1 + \dfrac{5}{4}\right)\left(1 + \dfrac{7}{9}\right)...\left(1 + \dfrac{(2n + 1)}{n^2}\right) \text{ is equal to}$$

(a) $\dfrac{(n + 1)^2}{2}$
(b) $\dfrac{(n + 1)^3}{3}$
(c) $(n + 1)^2$
(d) None of these

89. If a, b, c are in arithmetic progression, then the value of $(a + 2b - c)(2b + c - a)(a + 2b + c)$ is

(a) $16abc$ (b) $4abc$

(c) $8abc$ (d) $3abc$

90. If $y = \sin^{-1} x$, then its differential equation is

(a) $(1 - x^2)\dfrac{d^2 y}{dx^2} - x\dfrac{dy}{dx} = 0$

(b) $\sqrt{(1 - x^2)}\dfrac{d^2 y}{dx^2} - x\dfrac{dy}{dx} = 0$

(c) $(1 - x^2)\dfrac{d^2 y}{dx^2} + x\dfrac{dy}{dx} = 0$

(d) $(1 + x^2)\dfrac{d^2 y}{dx^2} + x\dfrac{dy}{dx} = 0$

SOLUTIONS

PHYSICS

1. (d) : Magnetic field intensity at a distance r from the straight wire carrying current is

$$B = \frac{\mu_0 I}{2\pi r}$$

As area of loop, $A = a^2$

and magnetic flux $\phi = BA$ $\therefore$ $\phi = \dfrac{\mu_0 I a^2}{2\pi r}$

The induced emf in the loop is

$$|\varepsilon| = \left|\frac{d\phi}{dt}\right| = \left|\frac{d}{dt}\left(\frac{\mu_0 I a^2}{2\pi r}\right)\right|$$

$$|\varepsilon| = \frac{\mu_0 I a^2}{2\pi r^2}\frac{dr}{dt} = \frac{\mu_0 I a^2 v}{2\pi r^2}$$

where $v = \dfrac{dr}{dt}$ is velocity.

2. (c) : As the spring is compressed by 2 m with the application of a force of 200 N, hence its spring constant k is given by

$$k = \frac{F}{2} = \frac{200\,\text{N}}{2\,\text{m}} = 100\,\text{N m}^{-1}$$

Suppose l be the distance along the inclined plane which the mass travels before it comes to rest. Applying the conservation of energy,

$$\frac{1}{2}kx_1^2 = mgh = mgl\sin\theta$$

or $\dfrac{1}{2} \times 100 \times 4^2 = 20 \times 9.8 \times l \times \dfrac{1}{2}$
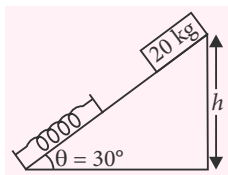
$\therefore$ $l = \dfrac{800}{98} = 8.16\,\text{m}$

3. (b) : As is clear from figure, path difference between the light waves reaching P from S_1 and S_2 is

$$\Delta x = 2\left(\frac{x}{2}\cos\theta\right) = x\cos\theta$$

For intensity to be maximum at P, path difference $\Delta x = n\lambda$, where $n = 0, 1, 2, ...$

$x\cos\theta = n\lambda$ or $\cos\theta = \dfrac{n\lambda}{x}$

As $\cos\theta$ cannot be greater than one, therefore,

$\dfrac{n\lambda}{x} \not> 1$ or $n \not> \dfrac{x}{\lambda}$

As $x = 5\lambda$, therefore, $n \not> \dfrac{5\lambda}{\lambda}$

i.e., $n \not> 5$ or $n = 1, 2, 3, 4, 5.$

Therefore, in all the four quadrants, there can be 20 maxima.
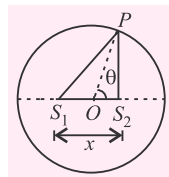
4. (d) : Given, $\dfrac{n_e}{n_h} = \dfrac{7}{5}$ and $\dfrac{I_e}{I_h} = \dfrac{7}{4}$

Drift velocity, $v_d = \dfrac{I}{nAe}$; $v_d \propto \dfrac{I}{n}$

$\therefore$ $\dfrac{(v_d)_e}{(v_d)_h} = \dfrac{I_e}{I_h} \times \dfrac{n_h}{n_e} = \dfrac{7}{4} \times \dfrac{5}{7} = \dfrac{5}{4}$

5. (d) : The given wave equation is

$$y = A\sin\left[\frac{2\pi}{\lambda}(vt - x)\right]$$

Wave velocity $= v$

Particle velocity,

$$v_p = \frac{dy}{dt} = A\frac{2\pi}{\lambda}v\cos\left[\frac{2\pi}{\lambda}(vt - x)\right]$$

Maximum particle velocity, $(v_p)_{\max} = \dfrac{2\pi}{\lambda}vA$

As per question $(v_p)_{\max} = 3v$

$$\frac{2\pi}{\lambda}vA = 3v$$

$$\lambda = \frac{2}{3}\pi A$$

6. (c) : Force on a negative charge $\vec{F} = -q_0\vec{E}$ is always directed towards the centre of ring and is variable as $E = \dfrac{1}{4\pi\varepsilon_0}\dfrac{qz_0}{(z_0^2 + R^2)^{3/2}}$.

Consequently, motion of charged particle will difinitely be periodic. Morever, if $z_o << R$, then

$$E = \frac{q}{4\pi\varepsilon_0 \cdot R^3} \cdot z_0 \quad \text{and} \quad F = \frac{-qq_0}{4\pi\varepsilon_0 \cdot R^3} \cdot z_0 \quad i.e.$$

$F \propto - z_0$. It shows that motion will be simple harmonic.

7. **(c) :** In first case, potential gradient, $K = \dfrac{\varepsilon_0}{l}$

where ε_0 is the emf of the battery in potentiometer circuit. As per question

$$\varepsilon = \frac{Kl}{5} = \frac{\varepsilon_0}{l} \times \frac{l}{5} = \frac{\varepsilon_0}{5}$$

In second case, length of potentiometer wire

$$= l + \frac{l}{2} = \frac{3l}{2}$$

Potential gradient, $K' = \dfrac{\varepsilon_0}{3l/2} = \dfrac{2\varepsilon_0}{3l}$

If l' is the new balancing length, then

$$\varepsilon = \frac{\varepsilon_0}{5} = \frac{2\varepsilon_0}{3l} \times l' \quad \text{or} \quad l' = \frac{3}{10} l$$
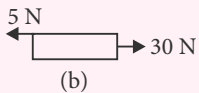
8. **(a) :** Maximum frictional force between the block and the plank is

$$f_{max} = \mu mg = (0.5)(1)(10) = 5 \text{ N}$$

The free body diagrams of the block and the plank are as shown in the figure (a) and (b) respectively.

Acceleration of block,

$$a_1 = \frac{5}{1} = 5 \text{ ms}^{-2}$$

Acceleration of plank, $a_2 = \dfrac{30-5}{2} = \dfrac{25}{2} \text{ m s}^{-2}$

∴ Relative acceleration of plank

$$a = a_2 - a_1$$

$$a = \frac{25}{2} - 5 = 7.5 \text{ m s}^{-2}$$

∴ $t = \sqrt{\dfrac{2S}{a}} = \sqrt{\dfrac{2\times 2}{7.5}} = 0.73 \text{ s}$

9. **(a) :**
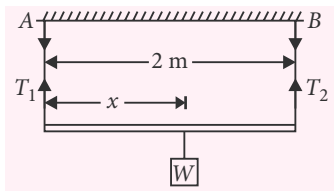
As stresses are equal, $\dfrac{T_1}{A_1} = \dfrac{T_2}{A_2}$ i.e.

$$\frac{T_1}{T_2} = \frac{A_1}{A_2} = \frac{0.1}{0.2} \quad \text{or} \quad T_2 = 2T_1 \quad \text{...(i)}$$

Now for translatory equilibrium of the rod,

$$T_1 + T_2 = W \quad \text{...(ii)}$$

From (i) and (ii), we get

$$T_1 = \frac{W}{3}; \; T_2 = \frac{2W}{3}$$

Now if x is the distance of weight W from steel wire, then for rotational equilibrium of rod,

$$T_1 x = T_2(2 - x) \quad \text{or} \quad \frac{W}{3}x = \frac{2W}{3}(2-x)$$

∴ $x = \dfrac{4}{3}$ m

10. **(c) :** Here, $r = \dfrac{6}{2} = 3$ cm, $t = 3$ mm $= 0.3$ cm

If R is radius of curvature of convex surface, then $2Rt = r^2$

$$R = \frac{r^2}{2t} = \frac{3\times 3}{2\times 0.3} = 15 \text{ cm}$$

As $\dfrac{1}{f} = (\mu - 1)\left(\dfrac{1}{R_1} - \dfrac{1}{R_2}\right)$

and $\mu = \dfrac{c}{v} = \dfrac{3\times 10^8}{2\times 10^8} = \dfrac{3}{2}$

∴ $\dfrac{1}{f} = \left(\dfrac{3}{2} - 1\right)\left(\dfrac{1}{\infty} - \dfrac{1}{-15}\right) = \dfrac{1}{30}$

$f = 30$ cm

11. **(b) :** As no external torque acts on the system, its angular momentum is conserved. Since there is no loss of energy due to friction, the total energy is conserved. However, the ring acquires some translational kinetic energy as it slides outwards, and hence rotational kinetic energy is not conserved.

12. **(b) :** The vertical force due to surface tension at the hole is

$(T\cos\theta)L = (T\cos\theta)2\pi r$ and it would balance the weight mg of the drop

$$m = \pi r^2 \rho h$$

$\Rightarrow \quad T\cos\theta(2\pi r) = \pi r^2 h\rho g$

$\Rightarrow \quad h = \dfrac{2T\cos\theta}{\rho rg}$
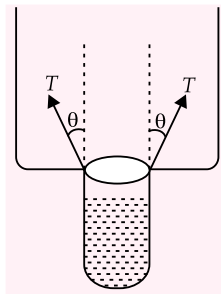
h is maximum when $\cos\theta = 1$

$$\Rightarrow \quad h_{\max} = \frac{2 \times 75 \times 10^{-3}}{10^3 \times 5 \times 10^{-4} \times 10} = 0.03 \text{ m} = 3 \text{ cm}$$

13. (b) : Pressure exerted by absorbed light

$$= \frac{1}{2}\left(\frac{I}{c}\right)$$

Pressure exerted by reflected light $= \frac{1}{2}\left(\frac{2I}{c}\right)$

Total radiation pressure on the surface is

$$P_{\text{rad}} = \frac{\frac{3}{2}I}{c} = \frac{1.5 \times 10^3}{3 \times 10^8} = 5 \times 10^{-6} \text{ Pa}$$

14. (b) : The acceleration of the electron is

$$a_e = \frac{eE}{m_e} \qquad \text{...(i)}$$

Starting from rest, the distance travelled by the electron in time t_1 in a uniform electric field E is

$$d = \frac{1}{2}a_e t_1^2 \text{ or } t_1 = \sqrt{\frac{2d}{a_e}} \qquad \text{...(ii)}$$

The acceleration of the proton is

$$a_p = \frac{eE}{m_p} \qquad \text{...(iii)}$$

Starting from rest, the same distance d travelled by the proton in time t_2 in the same electric field is

$$d = \frac{1}{2}a_p t_2^2 \text{ or } t_2 = \sqrt{\frac{2d}{a_p}} \qquad \text{...(iv)}$$

Divide (iv) by (iii), we get

$$\therefore \quad \frac{t_2}{t_1} = \sqrt{\frac{a_e}{a_p}} = \sqrt{\frac{m_p}{m_e}} \qquad \text{(Using (i) and (iii))}$$

15. (d) : Discharge per second through, $A = Sv_A$

Discharge per second through, $B = Sv_B$

Force of reaction at $A = \rho S v_A^2$

Similarly, force of reaction at $B = \rho S v_B^2$

Net force $F = \rho S\left(v_A^2 - v_B^2\right)$ ...(i)

By Bernoulli's theorem, if P_a is atmospheric pressure
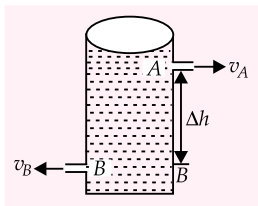
$$P_a + h\rho g + \frac{1}{2}\rho v_A^2 = P_a + (h + \Delta h)\rho g + \frac{1}{2}\rho v_B^2$$

$$\frac{1}{2}\left(v_A^2 - v_B^2\right) = \Delta h g \qquad \text{...(ii)}$$

Substitute, $v_A^2 - v_B^2 = \dfrac{F}{\rho S}$ in equation (ii)

$$\frac{1}{2}\left(\frac{F}{\rho S}\right) = \Delta h g \text{ or } F = 2\Delta h \rho g S$$

16. (a) : $\omega = 2\pi\upsilon = \sqrt{\dfrac{k}{m}}$

$$\therefore \quad k = (2\pi\upsilon)^2 m \qquad \text{...(i)}$$

Total energy of oscillation is

$$E = 0.5 \text{ J} + 0.4 \text{ J} = 0.9 \text{ J}$$

$$\because \quad E = \frac{1}{2}kA^2$$

where A is the amplitude of oscillation

$$\therefore \quad 0.9 = \frac{1}{2}kA^2$$

or $A = \sqrt{\dfrac{1.8}{k}} = \sqrt{\dfrac{1.8}{(2\pi\upsilon)^2 m}}$ (Using (i))

$$= \frac{1}{2\pi\upsilon}\sqrt{\frac{1.8}{0.2}} = \frac{1}{2\pi\left(\dfrac{25}{\pi}\right)}\sqrt{\frac{1.8}{0.2}} = \frac{3}{50} \text{ m} = 6 \text{ cm}$$

17. (c) : Energy of a photon $E = \dfrac{hc}{\lambda}$

or $E \propto \dfrac{1}{\lambda} \quad \therefore \quad \dfrac{E_2}{E_1} = \dfrac{\lambda_1}{\lambda_2}$

or $E_2 = E_1 \times \dfrac{\lambda_1}{\lambda_2} = 1.23 \times \dfrac{10000}{5000} = 2.46 \text{ eV}$

According to Einstein's photoelectric equation

$$h\upsilon - \phi_0 = \frac{1}{2}mv_{\max}^2 = eV_s$$

or $\phi_0 = h\upsilon_2 - eV_s = E_2 - eV_s$
$$= 2.46 - 1.36 = 1.10 \text{ eV}$$

18. (b) : Let T be the temperature at the junction.

Let L and A be the length and area of cross-section of each rod respectively.

$\therefore$ Heat current from Y to X is

$$H_1 = \frac{KA(90°C - T)}{L}$$

19. (a) : Fundamental frequency of an open organ pipe is

$$\nu_0 = \frac{v}{2l} = \frac{330 \text{ m s}^{-1}}{2 \times 0.3 \text{ m}} = 550 \text{ Hz}$$

The given frequency

$$\nu = 1.1 \text{ kHz} = 1100 \text{ Hz} = 2\nu_0$$

Therefore, the given frequency corresponds to 2nd harmonic.

20. (b) : Output of $G_1 = \overline{(A + B)}$

Output of $G_2 = \overline{A \cdot B}$

Output of $G_3 = (A + B) \cdot \overline{A \cdot B}$

which gives XOR gate.

21. (b) :
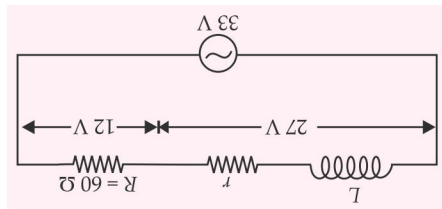
Let r be the resistance of the coil.

Current in the circuit,

$$I = \frac{12 \text{ V}}{60 \ \Omega} = 0.2 \text{ A}$$

According to voltage formula

$$27^2 = V_L^2 + V_r^2 \qquad \text{...(i)}$$
$$33^2 = V_L^2 + (V_R + V_r)^2 \qquad \text{...(ii)}$$

Subtract (i) from (ii), we get

$$33^2 - 27^2 = V_R^2 + V_r^2 + 2V_R V_r - V_r^2$$
$$33^2 - 27^2 = 12^2 + 2 \times 12 \times V_r$$
$$V_r = \frac{33^2 - 27^2 - 12^2}{(2 \times 12)} = 9 \text{ V}$$
$$V_r = Ir \Rightarrow r = \frac{V_r}{I} = \frac{9 \text{ V}}{0.2 \text{ A}} = 45 \ \Omega$$

Heat current from Z to X is $H_2 = \dfrac{KA(90°C - T)}{L}$

Heat current from X to W is

$$H_3 = \frac{KA(T - 0°C)}{L}$$

At the junction X,

$$H_1 + H_2 = H_3$$
$$\therefore \quad 90°C - T + 90°C - T = T$$

or $3T = 180°C$ or $T = 60°C$

22. (d) : $W = T\Delta A = T(2 \times 4\pi R^2)$

and $V = \dfrac{4}{3}\pi R^3$

When volume is doubled new radius becomes

$$R' = (2)^{1/3}R$$
$$\therefore \ W' = T \times 2 \times 4\pi R'^2 = T \times 2 \times 4\pi (2)^{2/3} R^2$$
$$= T \times 2 \times 4\pi (4)^{1/3} R^2 = (4)^{1/3} W$$

23. (b) : If I_0 is intensity of unpolarised light, then intensity of polarised light from 1st polaroid

$$= \frac{I_0}{2}$$

On rotation through 45°, intensity of light from 2nd polaroid,

$$I = \left(\frac{I_0}{2}\right)(\cos 45°)^2 = \frac{I_0}{2}\left(\frac{1}{\sqrt{2}}\right)^2 = \frac{I_0}{4}$$
$$= 25\% \text{ of } I_0$$

24. (c) : When charge of amount q has flown from A to B, the charge on A is $(Q - q)$.

The potentials of A and B are

$$V_A = \frac{1}{4\pi\varepsilon_0}\frac{Q-q}{r} + \frac{1}{4\pi\varepsilon_0}\frac{q}{R}$$
$$V_B = \frac{1}{4\pi\varepsilon_0}\frac{Q-q}{R} + \frac{1}{4\pi\varepsilon_0}\frac{q}{R}$$
$$\therefore \quad V_A - V_B = \frac{1}{4\pi\varepsilon_0}(Q-q)\left(\frac{1}{r} - \frac{1}{R}\right) > 0$$
$$\therefore \quad V_A > V_B \text{ for all values of } q.$$

Charge will flow A to B till $q = Q$.

25. (c) : To keep the centre of mass at the same position, velocity of centre of mass is zero, so

$$\frac{m_1\vec{v_1} + m_2\vec{v_2}}{m_1 + m_2} = 0$$

[where $\vec{v_1}$ and $\vec{v_2}$ are velocities of particles 1 and 2 respectively.]

$$\Rightarrow m_1\frac{d\vec{r_1}}{dt} + m_2\frac{d\vec{r_2}}{dt} = 0$$
$$\left[\because \vec{v_1} = \frac{d\vec{r_1}}{dt} \text{ and } \vec{v_2} = \frac{d\vec{r_2}}{dt}\right]$$
$$\Rightarrow m_1 d\vec{r_1} + m_2 d\vec{r_2} = 0 \quad [d\vec{r_1} \text{ and } d\vec{r_2} \text{ represent the changes in displacement of particle.}]$$

Let 2nd particle has been displaced by distance x.

$$\Rightarrow m_1(d) + m_2(x) = 0$$
$$x = -\frac{m_1 d}{m_2}$$

–ve sign shows that both the particles have to move in opposite directions

So, $\dfrac{m_1 d}{m_2}$ is the distance moved by 2nd particle to keep centre of mass at the same position.

26. (a) : Let t be time for the potential of metal sphere to rise by 1 V.

β-particles emitted in this time
$$= (6.25 \times 10^{10}) \times t$$

Number of β-particles escaped in this time
$$= \left(\dfrac{80}{100}\right) \times (6.25 \times 10^{10})t = 5 \times 10^{10} t$$

∴ Charge acquired by the sphere in time t.
$$Q = (5 \times 10^{10} t) \times (1.6 \times 10^{-19})$$
$$= 8 \times 10^{-9} t \text{ C} \qquad \qquad ...(i)$$

(∵ Emission of β-particle lends to a charge e on metal sphere)

The capacitance C of a metal sphere is given by
$$C = 4\pi\varepsilon_0 \times r$$
$$= \left(\dfrac{1}{9 \times 10^9}\right) \times \left(\dfrac{10^{-3}}{2}\right) = \dfrac{10^{-12}}{18} \text{ F}$$

As $Q = C \times V$

Here $V = 1$ V

∴ $(8 \times 10^{-9})t = \left(\dfrac{10^{-12}}{18}\right) \times 1$

Solving it for t, we get $t = 6.95 \ \mu s$

27. (b) : For a rigid diatomic molecule, the translational degrees of freedom is 3 and the rotational degrees of freedom is 2 and the total degrees of freedom is 5. Thus, the rotational kinetic energy of one mole is

$$KE_{Rotational} = 2 \times \dfrac{1}{2} RT = RT$$

The total kinetic energy of one mole is

$$KE_{Total} = 5 \times \dfrac{1}{2} RT = \dfrac{5}{2} RT$$

Their ratio is $\dfrac{KE_{Rotational}}{KE_{Total}} = \dfrac{RT}{\dfrac{5}{2}RT} = \dfrac{2}{5}$

28. (b) : The smallest frequency and largest wavelength in ultraviolet region will be for transition from $n_2 = 2$ to $n_1 = 1$

∴ $\dfrac{1}{\lambda_{max}} = R\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

$\Rightarrow \quad \dfrac{1}{\lambda_{max}} = R\left[\dfrac{1}{1^2} - \dfrac{1}{2^2}\right] = R\left[1 - \dfrac{1}{4}\right] = \dfrac{3R}{4}$ ...(i)

The highest frequency and smallest wavelength for infrared region will be for transition from $n_2 = \infty$ to $n_1 = 3$

∴ $\dfrac{1}{\lambda_{min}} = R\left(\dfrac{1}{3^2} - \dfrac{1}{\infty}\right) = \dfrac{R}{9}$ ...(ii)

Divide (i) by (ii), we get

$$\dfrac{\lambda_{min}}{\lambda_{max}} = \dfrac{3R}{4} \times \dfrac{9}{R} = \dfrac{27}{4}$$

$$\lambda_{min} = \dfrac{27}{4} \times \lambda_{max}$$

$$= \dfrac{27}{4} \times 122 \text{ nm} = 823.5 \text{ nm}$$

29. (b) : The energy of the launching vehicle on the surface of the earth is

$$E_s = KE + PE = 0 + \left(-\dfrac{GMm}{R}\right) = -\dfrac{GMm}{R}$$

The energy of the vehicle in an orbit of radius r is

$$E_o = \dfrac{1}{2} m v_o^2 + \left(-\dfrac{GMm}{r}\right)$$
$$= \dfrac{1}{2} m \left(\dfrac{GM}{r}\right) - \dfrac{GMm}{r} \qquad \left[\text{As } v_o = \sqrt{\dfrac{GM}{r}}\right]$$
$$= -\dfrac{GMm}{2r}$$

The minimum energy required to spent the vehicle from the surface of earth to the orbit of radius $7R$ is

$$\Delta E = E_o - E_s$$
$$= -\dfrac{GMm}{2(7R)} - \left[-\dfrac{GMm}{R}\right]$$
$$= -\dfrac{GMm}{14R} + \dfrac{GMm}{R} = \dfrac{13}{14} \dfrac{GMm}{R}$$

30. (a) : $\Delta W_{AB} = P\Delta V = (10 \text{ N m}^{-2})(2 - 1) \text{ m}^3 = 10 \text{ J}$

$\Delta W_{BC} = 0 \qquad$ (As V = constant)

From first law of thermodynamics
$$\Delta Q = \Delta W + \Delta U$$
$$\Delta U = 0 \qquad \text{(As process } ABCA \text{ is cyclic)}$$

∴ $\Delta Q = \Delta W_{AB} + \Delta W_{BC} + \Delta W_{CA}$

∴ $\Delta W_{CA} = \Delta Q - \Delta W_{AB} - \Delta W_{BC} = 5 \text{ J} - 10 \text{ J} - 0$
$$= -5 \text{ J}$$

CHEMISTRY

31. (d) : Chlorine, being only a slightly stronger oxidising agent than bromine cannot oxidise it to +7 oxidation state as is required for the formation of the compound $BrCl_7$.

32. (c) :

$$CH_3NH_2 + OHC-\underset{\underset{\text{2-Methylbutanal}}{}}{\overset{\overset{CH_3}{|}}{CH}}-CH_2CH_3$$
$$\underset{\text{Methylamine}}{}$$

$$\xrightarrow{H_2/Pd} CH_3NH-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2CH_3$$
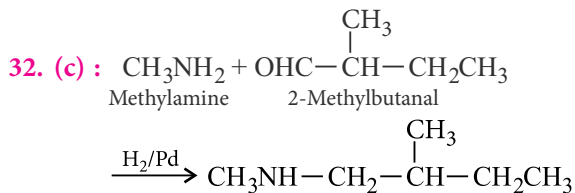
33. (b) : Protective power $\propto \dfrac{1}{\text{Gold number}}$

∴ Order of protective power will be
Gelatin > Haemoglobin > Sodium acetate
(0.005)　　　(0.05)　　　(0.7)

34. (b) : The alkali metal ions exist as hydrated ions $M^+(H_2O)_n$ in the aqueous solution. The degree of hydration, decreases with ionic size as we go down the group. Hence Li^+ ion is most hydrated e.g. $[Li(H_2O)_6]^+$. Since the mobility of ions is inversely proportional to the size of their hydrated ions, hence the increasing order of ionic mobility is $Li^+ < Na^+ < K^+ < Rb^+$.

35. (a) : A compound containing one asymmetric carbon atom exists in two stereoisomers which are known as enantiomers and are mirror images of each other.
The pair of enantiomers with similar groups on the opposite site is called threo form.

36. (a) : Mass of one unit cell (m) = Volume × Density

$$= a^3 \times d = a^3 \times \frac{M \times Z}{N_0 a^3} = \frac{M \times Z}{N_0}$$

$$m = \frac{58.5 \times 4}{6.02 \times 10^{23}}\, g$$

∴ Number of unit cells in $1\, g = \dfrac{1}{m}$

$$= \frac{6.02 \times 10^{23}}{58.5 \times 4}$$
$$= 2.57 \times 10^{21}$$

37. (c) : The higher the charge on the metal ion, smaller is the ionic size and more is the complex forming ability. Thus, the degree of complex formation decreases in the order :
$$M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+.$$
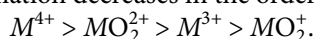
The higher tendency of complex formation of MO_2^{2+} as compared to M^{3+} is due to high concentration of charge on metal atom M in MO_2^{2+}.

38. (b) : $\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{\text{dil. NaOH}}$

$$\underset{\text{Cinnamaldehyde}}{C_6H_5CH=CHCHO}$$
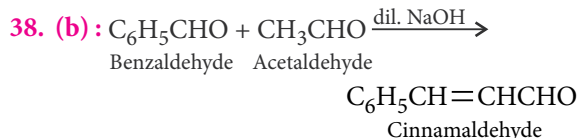
39. (a) : Concerned reaction is

$$\underset{100\, g}{CaCO_3} \xrightarrow{\Delta} \underset{56\, g}{CaO} + CO_2$$
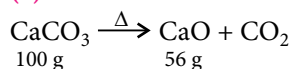
56 g of CaO is obtained from 100 g of $CaCO_3$

0.56 g of CaO is obtained from $\dfrac{100}{56} \times 0.56 = 1\, g$ of $CaCO_3$.

We know that,

$$\underset{111\, g}{CaCl_2} + Na_2CO_3 \rightarrow \underset{100\, g}{CaCO_3} + 2NaCl$$
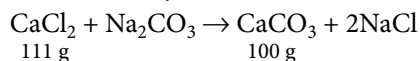
100 g of $CaCO_3$ is obtained from 111 g of $CaCl_2$
1 g of $CaCO_3$ is obtained from $\dfrac{111}{100} = 1.11\, g$ of $CaCl_2$

Weight of NaCl = 4.44 − 1.11 = 3.33 g

% age of NaCl $= \dfrac{3.33}{4.44} \times 100 = 75\%$

40. (b) : The chemical composition of
1. 　Malachite – $[CuCO_3 \cdot Cu(OH)_2]$
2. 　Azurite – $[Cu(OH)_2 \cdot 2CuCO_3]$
3. 　Chalcocite – Cu_2S
4. 　Verdigris –
$$Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_3 \cdot 2H_2O$$

41. (c) :

$$CH_3CN \xrightarrow{Na/C_2H_5OH} \underset{(X)}{CH_3CH_2NH_2} \underset{HNO_2}{\longrightarrow}$$

$$\underset{(Z)}{CH_3COOH} \underset{\text{Baeyer's reagent}}{\overset{MnO_4^-/OH^-}{\longleftarrow}} \underset{(Y)}{CH_3CH_2OH} \longleftarrow$$
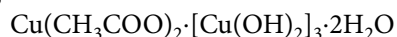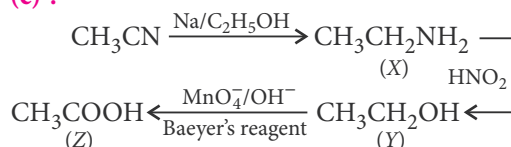
42. (b) : Sucrose decomposes according to first order rate law, hence

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}, t_{1/2} = 3\, hrs, t = 8\, hrs, \frac{[R]}{[R]_0} = ?$$

∵ $t_{1/2} = 3$ hrs, ∴ $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{3} = 0.231\, hr^{-1}$

Hence, $0.231 = \dfrac{2.303}{8} \log \dfrac{[R]_0}{[R]}$

or, 　$\log \dfrac{[R]_0}{[R]} = 0.8024$

or, $\dfrac{[R]_0}{[R]} = \text{Antilog}\,(0.8024) = 6.345$

or, $\dfrac{[R]}{[R]_0} = \dfrac{1}{6.345} = 0.158$

43. (b) : Metallic silver dissolves in sodium cyanide solution in the presence of oxygen to form water soluble complex *i.e.*, sodium argentocyanide.
$4Ag + 8NaCN + 2H_2O + O_{2(air)} \longrightarrow$
$$4Na[Ag(CN)_2] + 4NaOH$$
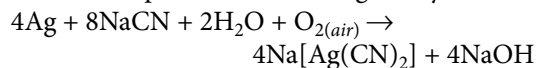
44. (d) : Camphor and benzoic acid both undergo sublimation hence chemical reagents are used to separate such mixtures.

45. (d) : Relation between root mean square velocity and temperature
$$u_{rms} = \sqrt{\dfrac{3RT}{M}}$$
$$u_{rms} \propto \sqrt{T}$$
$$T \propto u_{rms}^2$$
If u is doubled, T will become four times.

46. (c) : SO_2 and NO_2 when dissolve in water, form H_2SO_4 and HNO_3, (strong acids) respectively.
$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$
$$2SO_2 + O_2 \xrightarrow{\text{Particulate}} 2SO_3$$
$$SO_3 + H_2O \longrightarrow H_2SO_4$$
Thus, they cause the pollution by increasing acidity.
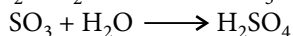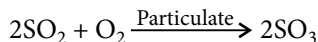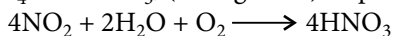
47. (d) :
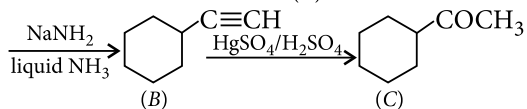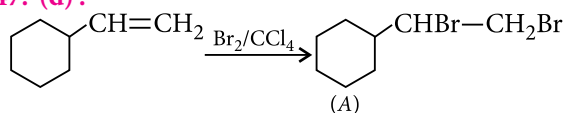
48. (b) : For endothermic reaction, $\Delta H = +ve$
Now, $\Delta G = \Delta H - T\Delta S$
ΔG will be +ve when ΔH and ΔS both are +ve and temperature is low so that $\Delta H > (-T\Delta S)$.
ΔG will be –ve when ΔH and ΔS both are +ve and temperature is high so that $\Delta H < (-T\Delta S)$.

49. (b) : $CH_3CH_2-O-N=O$ is a nitrite derivative.

50. (c) : The reactivity order of halides towards S_N2 reaction is
methyl > 1° > 2° > 3° > allyl > benzyl halides.

51. (c) : Suppose that $[Br^-]$ and $[Cl^-]$ are a and b respectively.
At equilibrium, $E_{cell} = 0$
$$\therefore\quad [Ag^+]_{LHS} = \dfrac{K_{sp(AgBr)}}{[Br^-]} = \dfrac{5\times10^{-13}}{a}$$
$$[Ag^+]_{RHS} = \dfrac{K_{sp(AgCl)}}{[Cl^-]} = \dfrac{1\times10^{-10}}{b}$$
$$E_{cell} = E^\circ_{Ag/Ag^+} + E^\circ_{Ag^+/Ag} + \dfrac{0.059}{1}\log\dfrac{[Ag^+]_{RHS}}{[Ag^+]_{LHS}}$$
$$0 = 0 + \dfrac{0.059}{1}\log\dfrac{1\times10^{-10}\times a}{5\times10^{-13}\times b}$$
$$\therefore\quad \dfrac{200a}{b} = \text{antilog}\,0 \quad\Rightarrow \dfrac{a}{b} = \dfrac{1}{200}$$

52. (d) : Cellophane is a semi-synthetic polymer.

53. (d) :
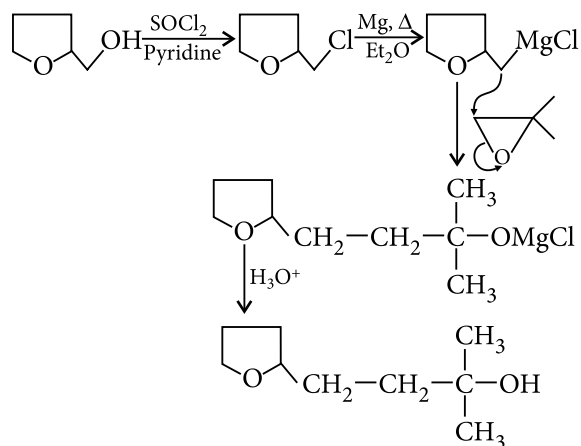
54. (c) :
$$SO_{2(g)} + NO_{2(g)} \rightleftharpoons SO_{3(g)} + NO_{(g)}$$

	SO_2	NO_2	SO_3	NO
Initial conc.	1.50 M	1.50 M	0	0
Conc. at equi.	1.50 – x	1.50 – x	x	x

$$K_c = \dfrac{[SO_3][NO]}{[SO_2][NO_2]} = \dfrac{x^2}{(1.50-x)^2} = 3.00$$
Taking square root of each side,
$$\dfrac{x}{1.50-x} = 1.73$$
$x + 1.73\,x = 2.595 \Rightarrow x = 0.951$
% of SO_2 converted into product
$$= \dfrac{0.951}{1.50} \times 100 = 63.4\%$$

55. (a) : Given reactions can be explained as follows:

$[Co(NH_3)_5Cl]Cl_2 \rightleftharpoons [Co(NH_3)_5Cl]^{2+} + 2Cl^-$
$\Rightarrow$ 3 ions.

$[Co(NH_3)_5Cl]Cl_2 + 2AgNO_3 \rightarrow$
$[Co(NH_3)_5Cl](NO_3)_2 + 2AgCl\downarrow$
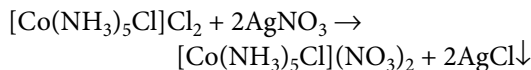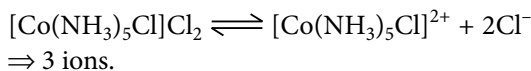
56. (d) : Proline has 2° amino group. Hence, it is not estimated by Van Slyke method.

57. (b) : For precipitation, $Q_{ip} > K_{sp}$

$Q_{ip} = [Ca^{2+}] [F^-]^2$

$= \left(\dfrac{10^{-2}}{2}\right) \times \left(\dfrac{10^{-3}}{2}\right)^2$

$= 1 \cdot 25 \times 10^{-9} > K_{sp}$,

Precipitate will be formed.

58. (d) : PbI_4 is least stable. Since Pb^{4+} is less stable in comparison to Pb^{2+} due to inert pair effect.

59. (a) : $CH \equiv CH \longrightarrow CH \equiv \bar{C}: + H^+$
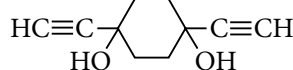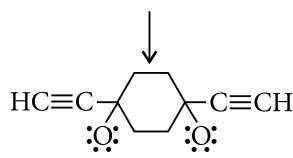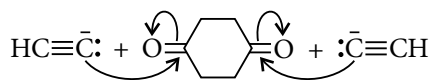
60. (a) : $\Delta T_f = iK_f m$ since K_f and m are constant $\Delta T_f \propto i$.

i is lowest for glucose ($i = 1$) and the lower the value of ΔT_f, higher is the freezing point.

MATHEMATICS

61. (b) : Let $4\{x\} = x + [x] = 2[x] + \{x\}$. Therefore $3\{x\} = 2[x]$. Since $0 \le \{x\} < 1$, we have $0 \le 3\{x\} < 3$ and therefore $0 \le 2[x] < 3$.

$\Rightarrow \quad [x] = 0$ or 1 and $\{x\} = 0$ or $\dfrac{2}{3}$

Therefore

$$x = 0 \text{ or } 4\left(\dfrac{2}{3}\right) = x + 1 \Rightarrow x = 0 \text{ or } \dfrac{5}{3}$$

62. (b) : Here $f(x)$ is defined for all real x, since $e^x + e^{|x|} \ne 0$ for all $x \in \mathbb{R}$. Also

$$f(x) = \begin{cases} 0 & \text{for } x \ge 0 \\ \dfrac{e^x - e^{-x}}{e^x + e^{-x}} = \dfrac{e^{2x} - 1}{e^{2x} + 1} & \text{for } x < 0 \end{cases}$$

Therefore, $f(x) = 1 - \dfrac{2}{e^{2x} + 1}$ for all $x < 0$

For $x < 0$, $y = f(x) \Leftrightarrow 0 \ge y = 1 - \dfrac{2}{e^{2x} + 1} > -1$

From this it follows that the range of f is $(-1, 0]$

63. (b) : Let $z = x + iy$. Then

$|z^2| + |z - 3|^2 + |z - 6i|^2$
$\quad = x^2 + y^2 + (x - 3)^2 + y^2 + x^2 + (y - 6)^2$
$\quad = 3(x^2 + y^2) - 6x - 12y + 45$
$\quad = 3[(x - 1)^2 + (y - 2)^2] + 30 \ge 30$

(equality holds when $z = 1 + 2i$). Therefore, the minimum value is 30.

64. (c) : By hypothesis,

$a\alpha^2 + b\alpha + c = 0$ and $a\beta^2 - b\beta - c = 0$

Let $\quad f(x) = \dfrac{a}{2} x^2 + bx + c$

Then, $f(\alpha) = \dfrac{a}{2}\alpha^2 + b\alpha + c = \dfrac{1}{2}(a\alpha^2 + 2b\alpha + 2c)$

$\qquad\qquad = \dfrac{1}{2}(a\alpha^2 - 2a\alpha^2) = -\dfrac{a}{2}\alpha^2$

and $\quad f(\beta) = \dfrac{a}{2}\beta^2 + b\beta + c$

$\qquad = \dfrac{1}{2}(a\beta^2 + 2b\beta + 2c) = \dfrac{1}{2}(a\beta^2 + 2a\beta^2) = \dfrac{3}{2}a\beta^2$

Therefore,

$$f(\alpha)f(\beta) = \dfrac{-a^2\alpha^2\beta^2}{4} < 0$$

Hence $f(x) = 0$ has a root in between α and β.

65. (a) : Given $(\cot \alpha_1) \cdot (\cot \alpha_2) \dots (\cot \alpha_n) = 1$

$\Rightarrow \displaystyle\prod_{i=1}^{n} \cos \alpha_1 = \prod_{i=1}^{n} \sin \alpha_1$

$\Rightarrow \displaystyle\prod_{i=1}^{n} \cos^2 \alpha_1 = \prod_{i=1}^{n} \sin \alpha_1 \cos \alpha_1 = \prod_{i=1}^{n} \dfrac{\sin 2\alpha_1}{2} \le \dfrac{1}{2^n}$

$\Rightarrow \displaystyle\prod_{i=1}^{n} \cos \alpha_1 \le \dfrac{1}{2^{n/2}}$

Hence, maximum value of $\displaystyle\prod_{i=1}^{n} \cos \alpha_1$ is $\dfrac{1}{2^{n/2}}$.

66. (d) : Let $\sqrt{3} + 1 = r \cos \alpha$, $\sqrt{3} - 1 = r \sin \alpha$

$\therefore \quad r^2 = (\sqrt{3} + 1)^2 + (\sqrt{3} - 1)^2 = 8$ or $r = 2\sqrt{2}$

and $\tan\alpha = \dfrac{\sqrt{3}-1}{\sqrt{3}+1} = \dfrac{1-\dfrac{1}{\sqrt{3}}}{1+\dfrac{1}{\sqrt{3}}}$

or $\tan\alpha = \tan(45° - 30°) = \tan 15°$

$\therefore \quad \alpha = 15° = \dfrac{\pi}{12}$

Using these in the given equation, we get

$r\cos(\theta - \alpha) = 2$

or $\cos\left(\theta - \dfrac{\pi}{12}\right) = \dfrac{2}{r} = \dfrac{2}{2\sqrt{2}} = \dfrac{1}{\sqrt{2}} = \cos\left(\dfrac{\pi}{4}\right)$

$\therefore \quad \theta - \dfrac{\pi}{12} = 2n\pi \pm \dfrac{\pi}{4}$ or $\theta = 2n\pi \pm \dfrac{\pi}{4} + \dfrac{\pi}{12}, n \in I$

67. (a) : $\dfrac{x+5}{\cos\theta} = \dfrac{y+4}{\sin\theta} = r_1 = AB$

$(r_1\cos\theta - 5, r_1\sin\theta - 4)$ lies on $x + 3y + 2 = 0$

$\therefore \quad r_1 = \dfrac{15}{\cos\theta + 3\sin\theta} \Rightarrow \dfrac{15}{AB} = \cos\theta + 3\sin\theta$

and similarly $\dfrac{10}{AC} = 2\cos\theta + \sin\theta$

and $\dfrac{6}{AD} = \cos\theta - \sin\theta$

Putting in the given relation, we get

$(2\cos\theta + 3\sin\theta)^2 = 0$

$\therefore \quad \tan\theta = -2/3 \Rightarrow y + 4 = -2/3\,(x + 5)$

68. (a) : $AB = 6, CD = 15$

Let $OA = a$ and $OC = b$
then $a \times (a + 6)$
$\qquad = OP^2 = 16$

$\Rightarrow \quad a^2 + 6a - 16 = 0$
$\Rightarrow \quad (a + 8)(a - 2) = 0$
$\Rightarrow \quad a = 2 \quad (\because a > 0)$
and $b(b + 15) = 16 \Rightarrow b^2 + 15b - 16 = 0$
$\Rightarrow \quad (b - 1)(b + 16) = 0 \Rightarrow b = 1 \qquad (\because b > 0)$

$\therefore \quad$ Centre of the circle is $\left(5, \dfrac{17}{2}\right)$.

Since circle passing through (0, 1), therefore,

radius $= \dfrac{5}{2}\sqrt{13}$

$\therefore \quad$ Equation of the required circle is

$(x - 5)^2 + \left(y - \dfrac{17}{2}\right)^2 = \dfrac{325}{4}$

$\Rightarrow \quad x^2 + y^2 - 10x - 17y + 16 = 0$
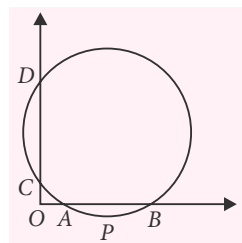
69. (d) : We have $a^2 = 25, b^2 = 16$

$\therefore e = \sqrt{1 - \dfrac{b^2}{a^2}} = \sqrt{1 - \dfrac{16}{25}} = \dfrac{3}{5}$. So, the coordinates of foci, S and S' are (3, 0) and (–3, 0) respectively. Let $P(5\cos\theta, 4\sin\theta)$ be a variable point on the ellipse. Then A = area of $\Delta PSS' = 12\sin\theta$.

70. (b) : $\sin^{-1}\left(\dfrac{142}{65\sqrt{5}}\right) = \tan^{-1}\left(\dfrac{142}{\sqrt{(65\sqrt{5})^2 - (142)^2}}\right)$

$\qquad\qquad = \tan^{-1}\left(\dfrac{142}{31}\right)$

$2\tan^{-1}\left(\dfrac{1}{5}\right) = \tan^{-1}\left(\dfrac{2/5}{1 - (1/25)}\right) = \tan^{-1}\left(\dfrac{5}{12}\right)$

$3\tan^{-1}\left(\dfrac{1}{2}\right) = \tan^{-1}\left(\dfrac{(3/2) - (1/8)}{1 - (3/4)}\right) = \tan^{-1}\left(\dfrac{11}{2}\right)$

Therefore the given sum equals

$\tan^{-1}\left(\dfrac{11}{2}\right) + \tan^{-1}\left(\dfrac{5}{12}\right) + \tan^{-1}\left(\dfrac{142}{31}\right)$

$= \pi + \tan^{-1}\left(\dfrac{(11/2) + (5/12)}{1 - (55/24)}\right) + \tan^{-1}\left(\dfrac{142}{31}\right)$

$= \pi - \tan^{-1}\left(\dfrac{142}{31}\right) + \tan^{-1}\left(\dfrac{142}{31}\right) = \pi$

71. (c) : Let $\vec{r} = (2\hat{i} + 4\hat{j} - 5\hat{k}) + (\lambda\hat{i} + 2\hat{j} + 3\hat{k})$

$\qquad\qquad = (2 + \lambda)\hat{i} + 6\hat{j} - 2\hat{k}$

$\vec{e}$ = unit vector in the direction of $\vec{r}$

$\qquad = \dfrac{(2 + \lambda)\hat{i} + 6\hat{j} - 2\hat{k}}{\sqrt{(2 + \lambda)^2 + 36 + 4}}$

Therefore

$\vec{e} \cdot (\hat{i} + \hat{j} + \hat{k}) = 1$

$\Rightarrow \quad (2 + \lambda) + 6 - 2 = \sqrt{(2 + \lambda)^2 + 40}$
$\Rightarrow \quad (\lambda + 6)^2 = (2 + \lambda)^2 + 40$
$\Rightarrow \quad 12\lambda + 36 = 4\lambda + 44 \Rightarrow 8\lambda = 8 \Rightarrow \lambda = 1$

72. (b) : Since the birth date of any person can fall in anyone of the 12 months, the number of total outcomes is 12^6. Let

E : Event that the birth dates of all 6 fall in two different months.

Number of possibilities of 6 person's birth dates to fall in two different months (say February and March) is $2^6 - 2$ (this 2 corresponds to either all their birth dates fall in February or all fall in March). The number of ways that we can select 2 months out of 12 is $^{12}C_2$. Therefore

$$P(E) = \frac{{}^{12}C_2(2^6 - 2)}{12^6} = \frac{66 \times 62}{12^6} = \frac{11 \times 31}{12^5} = \frac{341}{12^5}$$

73. (c) : We have $a^2 + b^2 + c^2 - ab - bc - ca$

$$= \frac{1}{2}[(a-b)^2 + (b-c)^2 + (c-a)^2] \geq 0$$

Therefore, $\dfrac{a^2 + b^2 + c^2}{ab + bc + ca} \geq 1$

Also, since a, b, c are the sides of a triangle, we have $|b - c| < a$, $|c - a| < b$ and $|a - b| < c$. Therefore

$(a - b)^2 + (b - c)^2 + (c - a)^2 < a^2 + b^2 + c^2$

$2(a^2 + b^2 + c^2) - 2(ab + bc + ca) < a^2 + b^2 + c^2$

$a^2 + b^2 + c^2 < 2(ab + bc + ca)$

$\dfrac{a^2 + b^2 + c^2}{ab + bc + ca} < 2$

74. (b) : We have, $f(x) = \dfrac{1}{1-x}$.

As at $x = 1$, $f(x)$ is not defined, $x = 1$ is a point of discontinuity of $f(x)$.

If $x \neq 1$, $f[f(x)] = f\left(\dfrac{1}{1-x}\right) = \dfrac{1}{1 - 1/(1-x)} = \dfrac{x-1}{x}$

$\therefore$ $x = 0$, 1 are points of discontinuity of $f[f(x)]$.

If $x \neq 0$, $x \neq 1$,

$$f[f\{f(x)\}] = f\left(\frac{x-1}{x}\right) = \frac{1}{1 - \dfrac{(x-1)}{x}} = x$$

75. (c) : $l_1 = \lim_{x \to 2^+} x + [x] = \lim_{h \to 0} 2 + h + [2 + h] = 4$

$l_2 = \lim_{x \to 2^-} (2x - [x]) = \lim_{h \to 0}\{2(2 - h) - [2 - h]\}$

$\quad = \lim_{h \to 0}\{2(2 - h) - 1\} = 4 - 1 = 3$

$l_3 = \lim_{x \to \frac{\pi}{2}} \dfrac{\cos x}{x - \dfrac{\pi}{2}} = -\lim_{x \to \frac{\pi}{2}} \sin x = -1$

[Using L–Hospital's rule]

Thus, $l_3 < l_2 < l_1$

76. (b) : We have, $f(x) = 3 \cos |x| - 6ax + b$

$\quad\quad\quad = 3 \cos x - 6ax + b$ [$\because \cos(-x) = \cos x$]

$\Rightarrow$ $f'(x) = -3 \sin x - 6a$

Since, $f(x)$ is an increasing function $\forall x \in R$

$\Rightarrow$ $f'(x) > 0$, $\forall x \in R$

$\Rightarrow$ $-3 \sin x - 6a > 0$, $\forall x \in R$

In particular, at $x = \dfrac{\pi}{2}$

$\quad -3 - 6a > 0 \Rightarrow a < -\dfrac{1}{2}$

77. (a) : We have

$(1 + x)^m(1 - x)^n = (1 + {}^mC_1 x + {}^mC_2 x^2 + ...) \times$
$\quad\quad\quad\quad\quad\quad\quad\quad (1 - {}^nC_1 x + {}^nC_2 x^2 + ...)$

Therefore coefficient of x is given by

$\quad {}^mC_1 - {}^nC_1 = m - n = 3$ ...(i)

Now coefficient of x^2 is

$\quad {}^mC_2 + {}^nC_2 - {}^mC_1 \cdot {}^nC_1 = -6$

$\quad m(m - 1) + n(n - 1) - 2mn = -12$

$\quad (m - n)^2 - (m + n) = -12$ ...(ii)

$\quad 9 - (m + n) = -12$ [Using (i)]

$\quad m + n = 21$ ...(iii)

Solving (i) and (iii), we get $m = 12$, $n = 9$.

78. (a) : We have,

$$\begin{bmatrix} 1 & 1 \\ 0 & 1 \end{bmatrix}\begin{bmatrix} 1 & 2 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 3 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 1+2 \\ 0 & 1 \end{bmatrix}$$

Again

$$\begin{bmatrix} 1 & 3 \\ 0 & 1 \end{bmatrix}\begin{bmatrix} 1 & 3 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 6 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 1+2+3 \\ 0 & 1 \end{bmatrix}$$

By induction,

$$\text{LHS} = \begin{bmatrix} 1 & \sum_{k=1}^{n} k \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 378 \\ 0 & 1 \end{bmatrix}$$

Therefore,

$\dfrac{n(n+1)}{2} = 378$ or $n(n + 1) = 27 \times 28$

Hence $n = 27$.

79. (a) : Let $I = \displaystyle\int_0^{\pi/2} \log\left(\frac{4 + 3\sin x}{4 + 3\cos x}\right) dx$

$= \displaystyle\int_0^{\pi/2} \log(4 + 3\sin x)dx - \int_0^{\pi/2} \log(4 + 3\cos x)dx$

$$\left[\because \log\frac{m}{n} = \log m - \log n\right]$$

$= \displaystyle\int_0^{\pi/2} \log\left[4 + 3\sin\left(\frac{\pi}{2} - x\right)\right]dx$

$\quad\quad\quad - \displaystyle\int_0^{\pi/2} \log(4 + 3\cos x)dx$

$= \displaystyle\int_0^{\pi/2} \log(4 + 3\cos x)dx - \int_0^{\pi/2} \log(4 + 3\cos x)dx$

$\therefore$ $I = 0$

Foundati⊙n Series

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UNIT-9 Principles Related to Practical Chemistry

PRACTICAL INORGANIC CHEMISTRY

- Preparation of inorganic compounds
- Qualitative salt analysis

TIPS TO REMEMBER

PREPARATION OF INORGANIC COMPOUNDS

- ❏ Mohr's salt and potash alum are addition compounds.
  - ○ They are formed when stoichiometric amounts of two or more stable compounds join together.
  - ○ They lose their identity in solution and are called double salts.

$$FeSO_4 \cdot 7H_2O + (NH_4)_2SO_4 \xrightarrow[\Delta]{\text{dil. } H_2SO_4}$$
$$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O + H_2O$$
<div align="center">Mohr's salt</div>

$$K_2SO_4 + Al_2(SO_4)_3 \cdot 18H_2O + 6H_2O \xrightarrow[\Delta]{\text{dil. } H_2SO_4}$$
$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$
<div align="center">Potash alum (or phitkari)</div>
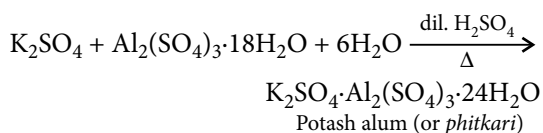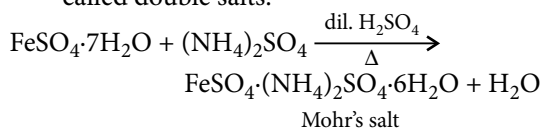
QUALITATIVE SALT ANALYSIS

Dry Tests

- ❏ **Preliminary Tests**
  - ○ *Colour* : NH_4^+, Pb^{2+}, Al^{3+}, Zn^{2+}, Ba^{2+}, Ca^{2+}, Sr^{2+}, Mg^{2+} (white), Cu^{2+} (blue), Ni^{2+}, Cr^{3+} (green), Fe^{2+} (light green), Fe^{3+} (brown), Co^{2+} (pink), Mn^{2+} (light pink or flesh colour)
  - ○ *Odour* : NH_4^+ (ammoniacal smell), CH_3COO^- (smell of vinegar), S^{2-} (smell of rotten eggs)

- ❏ **Dry Heating Test**

Observation	Radicals
Gas evolved	
Colourless	CO_3^{2-}, SO_3^{2-}, S^{2-}, Cl^-
Brown	Br^-, NO_3^-
Violet	I^-
Residue	
Yellow when hot, white when cold	Zn^{2+}
Brown when hot, yellow when cold	Pb^{2+}
Reddish brown	Fe^{2+}
Black	Ni^{2+}, Co^{2+}, Mn^{2+}, Cu^{2+}
Change in colour of salt	
Blue to white	$CuSO_4 \cdot 5H_2O$
Pink to blue	$CoCl_2$
Green to yellow	Ni^{2+} salt
Blue/green to brown/black	Cu^{2+} salt
Sound produced	
Crackling sound	NaCl, KI, $Pb(NO_3)_2$, $Ba(NO_3)_2$

- **Flame Test :** Salt with 1 or 2 drops of conc. HCl is introduced in the non-luminous (oxidising part) flame of the Bunsen burner using platinum wire. Some basic radicals impart characteristic colour to the flame.

Colour of flame	Radicals
Golden yellow	Na^+
Lilac or violet	K^+
Brick red	Ca^{2+}
Apple green	Ba^{2+}, Mo^{2+}
Crimson red	Sr^{2+}
Greenish blue	Cu^{2+}, BO_3^{3-}, Ti^{3+}

- **Borax Bead Test :** Coloured salts are heated on the glassy bead, coloured metaborates are formed.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow[\text{Pt wire}]{\Delta} Na_2B_4O_7 \xrightarrow{\Delta}$$
$$\underbrace{2NaBO_2 + B_2O_3}_{\text{Colourless glassy bead}}$$

Borax

In oxidising flame :
$$CuSO_4 + B_2O_3 \longrightarrow \underset{\substack{\text{Copper metaborate} \\ \text{(Blue)}}}{Cu(BO_2)_2} + SO_3$$

In reducing flame :
$$2Cu(BO_2)_2 + C \longrightarrow \underset{\text{(Colourless)}}{2CuBO_2} + B_2O_3 + CO$$
$$2Cu(BO_2)_2 + 2C \longrightarrow \underset{\text{(Brown red)}}{2Cu} + 2B_2O_3 + 2CO$$
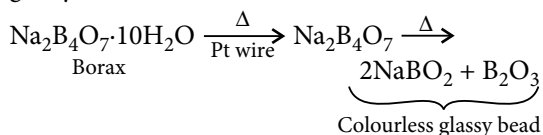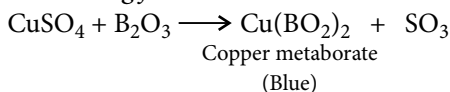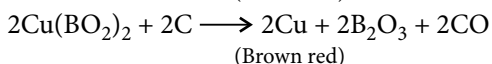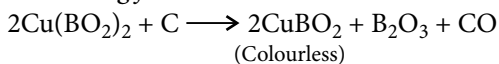
Hence different colours appear in different flames.

Metal	Colour in			
	Oxidising flame		Reducing flame	
	Hot	Cold	Hot	Cold
Cu	Green	Blue	Colourless	Brown red
Fe	Brown yellow	Pale yellow	Bottle green	Bottle green
Cr	Green	Green	Green	Green
Co	Blue	Blue	Blue	Blue
Mn	Violet	Amethyst red	Colourless	Colourless
Ni	Red brown	Brown	Grey	Grey

- **Charcoal Cavity Test (Reduction test) :** Salt is heated with fusion mixture (Na_2CO_3 and K_2CO_3) in a charcoal cavity in reducing flame to form metallic oxides which are left as coloured residues. The colour of the residue being characteristic of the basic radical present.

- **Cobalt Nitrate Test :** If the residue in charcoal cavity test is white, it is moistened with a drop of cobalt nitrate and on heating in an oxidising flame, colour of the residue changes.

$$ZnSO_4 + Na_2CO_3 \longrightarrow ZnCO_3 + Na_2SO_4$$
$$ZnCO_3 \longrightarrow ZnO + CO_2$$
$$2Co(NO_3)_2 \longrightarrow 2CoO + 4NO_2 + O_2$$
$$ZnO + CoO \longrightarrow \underset{\text{Rinmann's green}}{CoZnO_2}$$
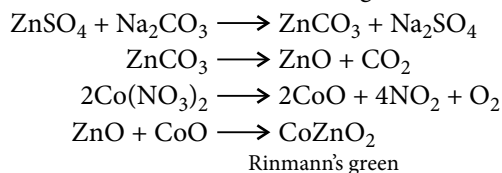
Observation	Inference
Blue mass	Aluminium
Green residue	Zinc
Pink residue	Magnesium
Bluish-green	Tin

🔑 KEY POINT

- Flame test should not be performed in the presence of As, Sb, Bi, Sn and Pb as these radicals form alloy with platinum and hence, the wire is spoiled.
- The yellow colouration due to sodium masks that of potassium. In such cases, view the flame through cobalt glass, the yellow sodium colour is absorbed and the potassium flame appears crimson.
- Cobalt nitrate test should be performed with 2-3 drops of cobalt nitrate solution otherwise black cobalt oxide is formed which will mask the colour of the residue.

MtG

Interested in more tests!

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Wet Tests

❑ **Identification of Acidic Radicals :**

- ○ *Group I acidic radicals :* Salt + dilute HCl or dilute H_2SO_4
  - – Effervescence or evolution of gases indicates the presence of group I acidic radicals.

Gas	Radical	Confirmatory Tests
CO_2 (Colourless, odourless gas)	Carbonate (CO_3^{2-})	$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2\uparrow$ Salt $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O$ Limewater White ppt. (milky) $CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$ Soluble
H_2S (Colourless gas with smell of rotten eggs)	Sulphide (S^{2-})	$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S\uparrow$ Salt $(CH_3COO)_2Pb + H_2S \longrightarrow PbS\downarrow + 2CH_3COOH$ Black ppt. $Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$ Sodium nitroprusside Violet

SO_2 (Colourless gas with suffocating odour having smell of burning sulphur)	Sulphite (SO_3^{2-})	$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2\uparrow$
		 Salt
		 $K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$
		      Green
		 $Na_2SO_3 + BaCl_2 \longrightarrow BaSO_3\downarrow + 2NaCl$
		      White ppt.
		 $BaSO_3 + 2HCl \longrightarrow BaCl_2 + H_2O + SO_2\uparrow$
		      Soluble

NO_2 (Brown gas)	Nitrite (NO_2^-)	$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$
		 Salt Nitrous acid
		 $3HNO_2 \longrightarrow H_2O + 2NO + HNO_3$
		 $2NO + O_2 \longrightarrow 2NO_2\uparrow$
		      Brown
		 $FeSO_4 \cdot 7H_2O + NO \longrightarrow [Fe(H_2O)_5NO]SO_4 + 2H_2O$
		      Brown

CH_3COOH (Colourless gas with smell of vinegar)	Acetate (CH_3COO^-)	$2CH_3COONa + H_2SO_4 \longrightarrow 2CH_3COOH + Na_2SO_4$
		 Salt
		 $3CH_3COONa + FeCl_3 \longrightarrow (CH_3COO)_3Fe + 3NaCl$
		      Blood red
		 $2CH_3COONa + \begin{matrix} COOH \\ | \\ COOH \end{matrix} \longrightarrow \begin{matrix} COONa \\ | \\ COONa \end{matrix} + 2CH_3COOH$
		      Smell of vinegar

🛈 KEY POINT

- SO_2 gas evolved from SO_3^{2-} ion, also turns limewater milky. Thus, for test of CO_3^{2-} ion, odour of gas should be carefully observed as SO_2 is a pungent gas while CO_2 is odourless gas.

- PbS, CdS, NiS, CoS, Sb_2S_3 and SnS are not decomposed by dil. H_2SO_4, therefore a pinch of zinc dust is added along with it. Conc. HCl should also be used.
- Carbonates of Bi and Ba are not easily decomposed by dil. H_2SO_4. Dil. HCl should be used.

○ *Group II acidic radicals* : Salt + conc. H_2SO_4 or conc. HCl and heat (if necessary)
  – Effervescence or evolution of gases indicates the presence of group II acidic radicals.

Gas	Radical	Observations and Reactions	Confirmatory Tests
HCl (Colourless gas with pungent smell) Cl_2 (Yellowish green, suffocating odour)	Chloride (Cl^-)	$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl\uparrow$ Salt $NH_4OH + HCl \longrightarrow NH_4Cl\uparrow + H_2O$ White dense fumes $HCl + AgNO_3 \longrightarrow AgCl\downarrow + HNO_3$ White ppt. $AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl +$ Soluble $2H_2O$ $2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4$ $+ MnSO_4 + 2H_2O + Cl_2\uparrow$	*Chromyl chloride test* : $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$ Salt (Conc.) $K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4$ $+ 2CrO_3 + H_2O$ $CrO_3 + 2HCl \longrightarrow CrO_2Cl_2\uparrow + H_2O$ Chromyl chloride (Deep red vapours) $CrO_2Cl_2 + 4NaOH \longrightarrow$ $Na_2CrO_4 + 2NaCl + 2H_2O$ Yellow colour $Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow$ $PbCrO_4\downarrow + 2CH_3COONa$ Yellow ppt.
Br_2 (Brown gas)	Bromide (Br^-)	$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$ Salt $2HBr + H_2SO_4 \longrightarrow Br_2\uparrow + 2H_2O + SO_2$ Brown $AgNO_3 + HBr \longrightarrow AgBr\downarrow + HNO_3$ Pale yellow ppt. $AgBr + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Br$ Soluble $+ 2H_2O$ $2NaBr + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4$ $+ MnSO_4 + 2H_2O + Br_2\uparrow$	*Layer test* : $2NaBr + $ dil. $H_2SO_4 + CHCl_3$ or CCl_4 Salt $+ Cl_2$ water $\longrightarrow 2NaCl + Br_2$ $Br_2 + CHCl_3 \longrightarrow$ Brown coloured or CCl_4 layer
I_2 (Deep violet gas)	Iodide (I^-)	$2KI + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$ Salt $2HI + H_2SO_4 \longrightarrow I_2\uparrow + SO_2 + 2H_2O$ Violet $AgNO_3 + HI \longrightarrow AgI\downarrow + HNO_3$ Yellow ppt. $AgI + NH_4OH \longrightarrow$ Not soluble $2KI + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4$ $+ MnSO_4 + 2H_2O + I_2\uparrow$	*Layer test* : $2NaI + Cl_2 \longrightarrow 2NaCl + I_2$ Salt $I_2 + $ Chloroform $\longrightarrow$ Violet coloured layer *Starch paper test* : $I_2 + $ Starch $\longrightarrow I_2$-starch complex Violet Blue colour vapours
NO_2 (Light brown gas having pungent smell)	Nitrate (NO_3^-)	$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$ Salt $4HNO_3 \longrightarrow 2H_2O + 4NO_2\uparrow + O_2$ Light brown fumes $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 +$ $2NO_2\uparrow + 2H_2O$	*Brown ring test* : $NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4$ Salt $+ HNO_3$ $6FeSO_4 + 2HNO_3 + 3H_2SO_4$(conc.) $\longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$ $[Fe(H_2O)_6]SO_4 \cdot H_2O + NO \longrightarrow$ Ferrous sulphate $[Fe(H_2O)_5NO]SO_4 + 2H_2O$ Brown ring

| $CO + CO_2$ (Colourless, odourless gas) | Oxalate $(C_2O_4^{2-})$ | $Na_2C_2O_4 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2C_2O_4$
 Salt
 $H_2C_2O_4 + [H_2SO_4] \longrightarrow CO + CO_2$
 Burns with   Turns lime <br> blue flame water milky
 $+ H_2O + [H_2SO_4]$ | $Na_2C_2O_4 + CaCl_2 \longrightarrow$
 Sodium carbonate $CaC_2O_4\downarrow + 2NaCl$
 extract   White ppt.
 $CaC_2O_4 + H_2SO_4(dil.) \longrightarrow$
 $H_2C_2O_4 + CaSO_4$
 $2KMnO_4(\text{few drops}) + 3H_2SO_4 \longrightarrow$
 Purple
 $K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$
 Colourless
 $\begin{array}{l}COOH \\ | \\ COOH\end{array} + [O] \longrightarrow 2CO_2 + H_2O$ |

KEY POINT

- With conc. H_2SO_4, group I radicals behave in the same way as with dil. H_2SO_4.
- Before testing CH_3COO^- ion with neutral $FeCl_3$ solution, make sure that the solution is free from CO_3^{2-}, SO_3^{2-}, PO_4^{3-} and I^- ions as they combine with Fe^{3+} ions.
- *Chromyl chloride test* :
  - Dry test tube should be used to prevent the hydrolysis of chromyl chloride vapours. $CrO_2Cl_2 + 2H_2O \longrightarrow H_2CrO_4 + 2HCl$
  - In case of chlorides of Hg, Sn, Ag, Pb and Sb, this test is performed by taking residue obtained after evaporation of sodium carbonate extract.
- Brown ring test is not reliable in the presence of NO_2^-, Br^-, I^- ions.

- While performing confirmatory test for $C_2O_4^{2-}$ ion, in presence of F^- ion, a white ppt. of CaF_2 is also formed by the addition of $CaCl_2$ solution. But CaF_2 does not dissolve in dil. H_2SO_4 and does not discharge the colour of $KMnO_4$.
- While performing layer test for Br^- and I^- ions, excess of Cl_2 water should be avoided.
  $Br_2 + Cl_2 \longrightarrow 2BrCl$
  Bromine monochloride
  (pale yellow colour)
  $Br_2 + 2H_2O + Cl_2 \longrightarrow 2HBrO + 2HCl$
  Hypobromous acid
  (colourless)
  $I_2 + 5Cl_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl$
  Iodic acid
  (colourless)

○ *Group III acidic radicals* : These radicals cannot be detected by either dil. H_2SO_4 or conc. H_2SO_4. For detection of these acidic radicals we need some specific tests.

Radical	**Observations and Reactions**
Sulphate (SO_4^{2-})	$Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4\downarrow + 2NaCl$ Salt White ppt. (insoluble in conc. HNO_3)
Phosphate (PO_4^{3-})	$Ca_3(PO_4)_2 + 6HNO_3 \longrightarrow 3Ca(NO_3)_2 + 2H_3PO_4$ Salt $H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow (NH_4)_3PO_4 \cdot 12MoO_3\downarrow + 21NH_4NO_3 + 12H_2O$ Ammonium molybdate Conc. Canary yellow ppt.
Borate (BO_3^{3-})	$2Na_3BO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2H_3BO_3$ Salt $H_3BO_3 + 3C_2H_5OH \longrightarrow (C_2H_5)_3BO_3\uparrow + 3H_2O$ Ethyl borate (burns with green edged flame)

Fluoride (F⁻)	$2NaF + H_2SO_4 \longrightarrow Na_2SO_4 + H_2F_2$
	   Salt Hydrofluoric acid
	$SiO_2 + 2H_2F_2 \longrightarrow SiF_4 + 2H_2O$
	  Silica Silicon tetrafluoride
	$3SiF_4 + 4H_2O \longrightarrow H_4SiO_4 + 2H_2SiF_6$
	                         Silicic acid
	                    (Gelatinous white)

🔑 KEY POINT

- Test for F⁻ ion should be performed in perfectly dry test tube, otherwise waxy white deposit will not be formed on the rod.
- $HgCl_2$ and NH_4Cl also produce a deposit under these conditions, but this deposit is crystalline in nature.

✓ SELF CHECK

1. $[X] + H_2SO_4 \longrightarrow [Y]$ a colourless gas with irritating smell,
$[Y] + K_2Cr_2O_7 + H_2SO_4 \longrightarrow$ green solution.
$[X]$ and $[Y]$ are
(a) SO_3^{2-}, SO_2 (b) Cl^-, HCl
(c) S^{2-}, H_2S (d) CO_3^{2-}, CO_2
(IIT-JEE 2003)

❑ **Identification of Basic Radicals**

   ○ *Separation of basic radicals into different groups* :

Basic radicals of	Group reagent	Precipitate as	Explanation
Group I Ag^+, Pb^{2+}, Hg_2^{2+}	dil. HCl	$AgCl, PbCl_2, Hg_2Cl_2$ (All white)	K_{sp} values of their chlorides are low, hence $K_{ip} > K_{sp}$ and they get precipitated.
Group II $Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, As^{3+}, Sb^{3+}, Sn^{2+}, Sn^{4+}$	H_2S in presence of dil. HCl	HgS, PbS, Bi_2S_3, CuS (Black), CdS, As_2S_3, SnS_2 (Yellow), Sb_2S_3 (Orange), SnS (Brown)	HCl (with common H^+ ion) decreases the ionization of H_2S which gives low $[S^{2-}]$. Hence, only group II sulphides having low K_{sp} values are precipitated.
Group III $Fe^{3+}, Cr^{3+}, Al^{3+}$	NH_4OH in presence of NH_4Cl	$Fe(OH)_3$ (Reddish brown), $Cr(OH)_3$ (Green), $Al(OH)_3$ (White)	NH_4Cl (with common NH_4^+ ion) decreases the ionization of NH_4OH giving low $[OH^-]$. Hence, only group III hydroxides having low K_{sp} values are precipitated.
Group IV $Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}$	H_2S in presence of NH_4OH	ZnS (Greenish white), MnS (Buff), CoS, NiS (Black),	Basic medium increases the ionization of H_2S, thus increasing $[S^{2-}]$, hence precipitation of group IV sulphides having high K_{sp} values occurs.
Group V $Ba^{2+}, Sr^{2+}, Ca^{2+}$	$(NH_4)_2CO_3$ in presence of NH_4OH	$BaCO_3, SrCO_3, CaCO_3$ (All white)	K_{sp} values of their carbonates are less than that of group VI (Mg^{2+}) hence, group V is precipitated before Mg^{2+}.
Group VI Mg^{2+}	Na_2HPO_4 in presence of NH_4OH	$Mg(NH_4)PO_4$ (White)	—
Zero NH_4^+	NaOH	Ammonia gas in evolved.	Tested independently from original solution.

○ *Confirmation of basic radicals of different groups* :

Precipitates of	Confirmatory Tests
Group I	
AgCl	Dissolves in NH_4OH, white ppt. of AgCl is again obtained on adding dil. HNO_3. Yellow ppt. of AgI is formed on adding KI.
$PbCl_2$	Dissolves in hot water, gives yellow ppt. of $PbCrO_4$ with K_2CrO_4 and yellow ppt. of PbI_2 with KI.
Hg_2Cl_2	Turns black with NH_4OH. Black residue $\{Hg + Hg(NH_2)Cl\}$ dissolves in aqua-regia.
Group II A	Precipitates do not dissolve in yellow ammonium sulphide.
HgS	Dissolves in aqua-regia, grey ppt. of Hg is obtained with $SnCl_2$ or Cu turnings.
PbS	Dissolves in dil. HNO_3, white ppt. of $PbSO_4$ is obtained on adding dil. H_2SO_4.
Bi_2S_3	Dissolves in dil. HCl, white ppt. of BiOCl is obtained on adding excess of water. Black ppt. of Bi is obtained on adding Na_2SnO_2 solution.
CuS	Blue coloured solution is obtained on adding dil. HNO_3 and excess of NH_4OH which gives chocolate brown ppt. of $Cu_2[Fe(CN)_6]$ with $K_4[Fe(CN)_6]$.
CdS	Colourless solution is obtained on adding dil. HNO_3 and excess of NH_4OH which gives yellow ppt. of CdS again on adding H_2S.
Group II B	Precipitates dissolve in yellow ammonium sulphide.
As_2S_3	Insoluble sulphide, As_2S_5 is obtained by treating with conc. HCl which gives yellow ppt. of ammonium arsenomolybdate on adding conc. HNO_3 and heating with ammonium molybdate.
SnS_2 or SnS	Filtrate of sulphide in conc. HCl is reduced to $SnCl_2$ by treating with Fe or Zn which, on adding $HgCl_2$ solution initially gives white ppt. of Hg_2Cl_2 and finally turns to grey Hg.
Sb_2S_3	Filtrate of sulphide in conc. HCl gives white ppt. of SbOCl on adding excess of water and orange ppt. of Sb_2S_3 on passing H_2S gas.
Group III	
$Fe(OH)_3$	Dissolves in dil. HCl, gives prussian blue solution or ppt. of $Fe_4[Fe(CN)_6]_3$ on adding $K_4[Fe(CN)_6]$ and blood red coloured $Fe(CNS)_3$ on adding KCNS.
$Cr(OH)_3$	The solution obtained on heating precipitate with NaOH and Br_2 water contains Na_2CrO_4 which gives yellow ppt. of $PbCrO_4$ on treating with acidified lead acetate solution.
$Al(OH)_3$	Dissolves in NaOH and is again precipitated out on boiling with NH_4Cl.
Group IV	Soluble in conc. HCl
ZnS	Solution $(ZnCl_2)$ is treated with NaOH, a white ppt. of $Zn(OH)_2$ appears which dissolves in excess of NaOH and on passing H_2S, white ppt. of ZnS is obtained.
MnS	Precipitate of MnO_2 is obtained on heating the solution with NaOH and Br_2 water. Pink colour of $HMnO_4$ is formed on supernatant liquid on treating the ppt. with excess of HNO_3 and red lead (Pb_3O_4).

Group IV	Insoluble in conc. HCl
CoS	Dissolves in aqua-regia. Yellow ppt. of potassium cobaltinitrite $K_3[Co(NO_2)_6]$ is obtained on adding CH_3COOH in excess and KNO_2.
NiS	Dissolves in aqua-regia. Red ppt. of Ni-dmg complex is obtained on adding NH_4OH in excess and dimethyl glyoxime.
Group V	Soluble in acetic acid
$BaCO_3$	Yellow ppt. of $BaCrO_4$ is obtained on adding K_2CrO_4 to solution.
$SrCO_3$	White ppt. of $SrSO_4$ is obtained on adding $(NH_4)_2SO_4$ to solution.
$CaCO_3$	White ppt. of CaC_2O_4 is obtained on adding $(NH_4)_2C_2O_4$.
Group VI	
Mg^{2+}	White ppt. of $Mg(NH_4)PO_4$ is formed on adding Na_2HPO_4 and NH_4OH to solution.
Zero	
NH_4^+	Salt evolves NH_3 gas on heating with NaOH which gives dense white fumes of NH_4Cl with HCl and a brown ppt. of $H_2N \cdot HgO \cdot HgI$ on adding Nessler's reagent, K_2HgI_4.

✓ **SELF** CHECK

2. Upon treatment with ammoniacal H_2S, the metal ion that precipitates as a sulphide is
   (a) Fe(III)   (b) Al(III)
   (c) Mg(II)   (d) Zn(II)

   (JEE Advanced 2013)

3. A solution of a metal ion when treated with KI gives a red precipitate which dissolves in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt(II) thiocyanate gives rise to deep blue crystalline precipitate. The metal ion is

   (a) Pb^{2+} (b) Hg^{2+}
   (c) Cu^{2+} (d) Co^{2+}

   (IIT-JEE 2007)

PRACTICAL ORGANIC CHEMISTRY

- Detection of extra elements in organic compounds
- Detection of functional groups in organic compounds
- Preparation of organic compounds

TIPS TO REMEMBER

QUALITATIVE ANALYSIS

❑ **Detection of Extra Elements (N, S, halogens) in Organic Compounds**

Element	Detection	Confirmatory test	Reactions
Nitrogen	Lassaigne's extract (L.E.) $Na + C + N \xrightarrow{\Delta} NaCN$ (L.E.)	L.E. + $FeSO_4$ + NaOH, boil and cool + $FeCl_3$ + conc. HCl Gives blue or green colour.	$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$ $Fe(OH)_2 + 6NaCN \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$ $Na_4[Fe(CN)_6] + FeCl_3 \xrightarrow{HCl} NaFe[Fe(CN)_6] + 3NaCl$ Prussian blue or $3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$ Prussian blue

Sulphur	$2Na + S \xrightarrow{\Delta} Na_2S$ (L.E.)	(i) L.E. + sodium nitroprusside A deep violet colour. (ii) L.E. + CH_3COOH + $(CH_3COO)_2Pb$ Gives a black ppt.	(i) $Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow$ Sodium nitroprusside $Na_4[Fe(CN)_5NOS]$ Deep violet (ii) $Na_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH}$ $PbS\downarrow + 2CH_3COONa$ Black ppt.
Halogens	$Na + Cl \xrightarrow{\Delta} NaCl$ (L.E.)	L.E. + HNO_3 + $AgNO_3$ (i) White ppt. soluble in aq. NH_3 (or NH_4OH) confirms Cl. (ii) Pale yellow ppt. partially soluble in aq. NH_3 (or NH_4OH) confirms Br. (iii) Yellow ppt. insoluble in aq. NH_3 (or NH_4OH) confirms I.	$NaX + AgNO_3 \xrightarrow{HNO_3} AgX\downarrow$ White ppt. $AgCl + 2NH_4OH_{(aq.)} \longrightarrow$ $[Ag(NH_3)_2]Cl + 2H_2O$ Soluble
Nitrogen and sulphur together	$Na + C + N + S \xrightarrow{\Delta}$ $NaSCN$ (L.E.) Sodium thiocyanate	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both.	$3NaSCN + FeCl_3 \longrightarrow$ $[Fe(SCN)_3] + 3NaCl$ Blood red colour

🔑 KEY POINT

- When sodium fusion is carried out with excess of sodium, thiocyanate decomposes to cyanide and sulphide ions which give their usual tests. Thus, we do not get blood red colour with ferric chloride even though N and S both are present.

$Na + C + N + S \longrightarrow NaCNS$
Sodium thiocyanate

$NaCNS + 2Na \longrightarrow NaCN + Na_2S$
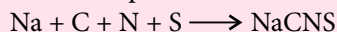
- Lassaigne's test fails in case of compounds which contain nitrogen but no carbon e.g., hydrazine (NH_2NH_2) and hydroxylamine (NH_2OH).

✓ SELF CHECK
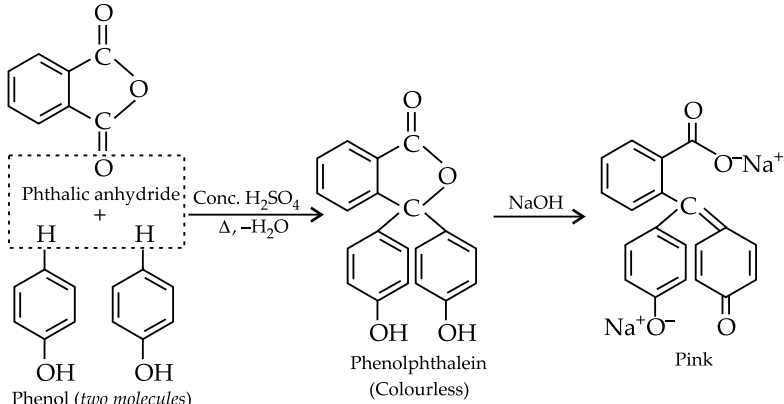
4. The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is
   (a) $Fe_4[Fe(CN)_6]_3$ (b) $Na_3[Fe(CN)_6]$
   (c) $Fe(CN)_3$ (d) $Na_4[Fe(CN)_5NOS]$
   (AIEEE 2004)

❑ **Detection of Functional Groups**

Test		Reaction	Confirmation
(A) Detection of unsaturation			
(i)	Baeyer's or KMnO$_4$ test	$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$ $>\!C\!=\!C\!< + H_2O + [O] \xrightarrow{OH^-} >\!\underset{\underset{OH}{\mid}}{C}\!-\!\underset{\underset{OH}{\mid}}{C}\!<$	Disappearance of pink colour of KMnO$_4$.
(iii)	Br$_2$ - CCl$_4$ test	$>\!C\!=\!C\!< + \underset{\underset{brown}{Red}}{Br_2} \xrightarrow{CCl_4} >\!\underset{\underset{Br}{\mid}}{\overset{\overset{Br}{\mid}}{C}}\!-\!C\!<$	Disappearance of brown colour.
(B) Detection of alcoholic group			
(i)	Ester test	$RCOOH + R'-OH \xrightarrow[-H_2O]{conc.\ H_2SO_4} \underset{Ester}{RCOOR'}$	Fruity smell of ester indicates – OH group.
(ii)	Ceric ammonium nitrate test	$2ROH + (NH_4)_2[Ce(NO_3)_6] \longrightarrow$ $\underset{Pink\ or\ red}{[(ROH)_2Ce(NO_3)_4]} + 2NH_4NO_3$	Appearance of pink or red colour.
(iii)	Xanthate test	$ROH + KOH_{(s)} \xrightarrow{\Delta} \underset{Pot.\ alkoxide}{RO^-K^+} + H_2O$ $RO^-K^+ + C\!\!\overset{\displaystyle S}{\underset{\displaystyle S}{\diagdown}} \longrightarrow \underset{\substack{Pot.\ alkyl\ xanthate \\ (Yellow\ ppt.)}}{R\!-\!O\!-\!C\!\!\overset{\displaystyle S^-K^+}{\underset{\displaystyle S}{\diagdown}}}$	Formation of yellow ppt.
(C) Detection of phenolic group			
(i)	FeCl$_3$ test	$FeCl_3 + 6C_6H_5OH \longrightarrow$ $\underset{Violet}{[Fe(OC_6H_5)_6]^{3-}} + 3H^+ + 3HCl$	Appearance of violet colouration.
(iI)	Azo dye test	$C_6H_5NH_2 + NaNO_2 + HCl \longrightarrow C_6H_5N_2^+Cl^-$ $C_6H_5N_2^+Cl^- + C_6H_5OH \xrightarrow[0\text{-}5°C]{pH\ 9\text{-}10}$ $p\text{-Hydroxyazobenzene}$	Formation of orange or red dye.
(iii)	Phthalein test or fluorescein test		
		Appearance of green, blue, pink, purple or red fluorescent solution.	

(iv)	Br$_2$-H$_2$O test		Appearance of white ppt.
(v)	Liebermann's nitroso test		
		Appearance of deep blue or green colour which turns red on dilution and again blue on adding sodium hydroxide solution.	

(D) Detection of carbonyl group

Aldehydic/Ketonic group

(i)	Brady's reagent (2, 4-DNP) test		Appearance of yellow, orange or red ppt.
(ii)	Sod. bisulphite test		Appearance of white ppt.

Aldehydic group

(i)	Tollens' test	$RCHO + 2[Ag(NH_3)_2]OH \longrightarrow RCOONH_4$ $+ 3NH_3 + H_2O + 2Ag_{(s)}$ Silver mirror	Formation of silver mirror along the sides of the test tube.
(ii)	Fehling's test	$RCHO + 2Cu^{2+} + 5OH^- \longrightarrow$ $2Cu^+\downarrow + RCOO^- + 3H_2O$ Red ppt.	A red ppt. is formed (only by aliphatic aldehydes).
(iii)	Schiff's test	$RCHO + p$-rosaniline hydrochloride (Colourless)	Appearance of pink colour.
(iv)	Benedict's test	$RCHO + 2Cu(OH)_2 + NaOH \longrightarrow RCOONa$ $+ Cu_2O\downarrow + 3H_2O$ Red ppt.	Appearance of red ppt.

		Ketonic group	
(i)	Iodoform test	$R – CO – CH_3 + 3I_2 + 4NaOH \longrightarrow$ $3NaI + CHI_3\downarrow + RCOONa + 3H_2O$ Yellow ppt.	Formation of yellow ppt. of CHI_3 (for methyl ketones only).
(ii)	Sodium nitroprusside test	$RCOR$ + sodium nitroprusside solution + NaOH	Appearance of wine-red colour.
(E) Detection of carboxylic group			
(i)	Litmus test	Blue litmus paper turns red.	–COOH group may be present.
(ii)	$NaHCO_3$ test	$RCOOH + NaHCO_3 \longrightarrow$ $RCOONa + H_2O + CO_2\uparrow$	Brisk effervescence of CO_2 indicates –COOH group.
(iii)	Ester test	$RCOOH + C_2H_5OH \xrightarrow[\Delta]{\text{Conc. } H_2SO_4}$ $RCOOC_2H_5 + H_2O$	Fruity smell of esters formed.
(iv)	$FeCl_3$ test	$3RCOOH + 3NH_4OH + FeCl_3 \longrightarrow$ $(RCOO)_3Fe + 3NH_4Cl + 3H_2O$ $\downarrow H_2O$ $Fe(OH)(OOCR)_2 + RCOOH$ Basic iron salt	Red : acetic acid, formic acid No colour change or light yellow colour : oxalic acid Violet : salicylic acid Buff : benzoic acid
(F) Detection of amino group			
		Primary amines	
(i)	Nitrous acid test	$R – NH_2 + HNO_2 \longrightarrow R – OH + N_2\uparrow + H_2O$	N_2 effervescence indicates 1° amino group.
(ii)	Carbylamine test	$R – NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta}$ $R – N \equiv C + 3KCl + 3H_2O$ Isocyanide	Offensive smell of isocyanide indicates 1° aliphatic or aromatic amino group.
(iii)	Azo dye test	$C_6H_5NH_2 + NaNO_2 + HCl \xrightarrow[\text{5-10 atm}]{\text{0-5°C}} C_6H_5N_2^+Cl^-$ Orange azo dye	A red or orange coloured dye confirms 1° aromatic amino group.
		Secondary amines	
(i)	Liebermann's nitroso test	 Nitrosoamine	Formation of a yellow oily nitrosoamine indicates 2° aliphatic or aromatic amino group.
(G) Detection of nitro group			
(i)	Mulliken Barker test	$RNO_2 + 4[H] \xrightarrow{Zn + NH_4Cl} RNHOH + H_2O$ $RNHOH + 2[Ag(NH_3)_2]OH \longrightarrow$ $RNO + 2H_2O + 4NH_3 + 2Ag\downarrow$ Grey black ppt.	Appearance of grey black ppt.
(ii)	Ferrous hydroxide test	$RNO_2 + 6Fe(OH)_2 + 4H_2O \longrightarrow$ Light green $\quad RNH_2 + 6Fe(OH)_3\downarrow$ Brown ppt.	Appearance of brown ppt.

❑ **Distinction Tests**

Test	Phenol	Alcohol
Blue litmus test	Turns red	✗
$FeCl_3$ test	Gives blue, violet, green or red colouration	✗
Azo dye test	Forms orange-red colour dye	✗
Br_2-water test	Gives white ppt.	✗

Test	Phenol	Carboxylic acid
$NaHCO_3$ test	✗	Gives brisk effervescence

Test	Aldehyde	Ketone
Tollens' test	Gives shiny silver mirror	✗
Fehling's solution test	Gives red ppt.	✗
Schiff's reagent test	Gives pink colour	✗
Reduction with $LiAlH_4$	Reduced to 1° alcohol	Reduced to 2° alcohol
Peroxy acid (Caro's acid, peroxy benzoic acid)	Acid is formed.	Ester is formed.

🐾 KEY POINT

- *Cerric ammonium test* :
  - Many aromatic amines which are easily oxidisable also give this test.
  - Some phenols also give green or brown ppt.
- *Ferric chloride test* : Also given by enols

$$\begin{bmatrix} \overset{\displaystyle OH}{\underset{\displaystyle |}{}} \\ -C=C- \end{bmatrix}$$

- *Sodium bisulphite test* :
  - Aliphatic aldehydes and methyl ketones which are not sterically hindered such as acetaldehyde, acetone, ethyl methyl ketone give this test.

  – Among aromatic aldehydes and ketones, only benzaldehyde gives this test but acetophenone, benzophenone do not give this test.
- *Iodoform test* : Only methyl ketones (ketones containing —$COCH_3$ group) give this test.
- $NaHCO_3$ *test* : Some phenols such as 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol (picric acid) also respond to this test.

✅ SELF CHECK

5. For the identification of β-naphthol using dye test, it is necessary to use
   (a) dichloromethane solution of β-naphthol
   (b) acidic solution of β-naphthol
   (c) neutral solution of β-naphthol
   (d) alkaline solution of β-naphthol.
   (JEE Advanced 2014)

6. Which of the following reagents may be used to distinguish between phenol and benzoic acid?
   (a) Aqueous NaOH   (b) Tollen's reagent
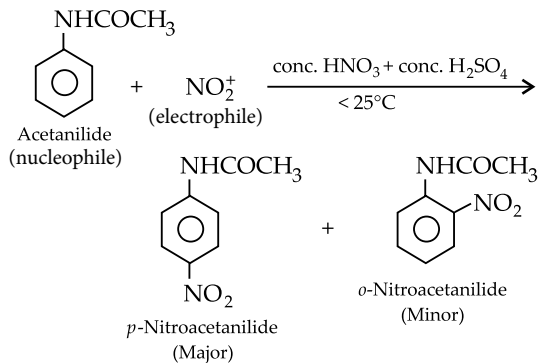   (c) Molisch reagent   (d) Neutral $FeCl_3$
   (AIEEE 2011)

PREPARATION OF ORGANIC COMPOUNDS

❑ **Acetanilide :** It is prepared by nucleophilic acyl substitution reaction.
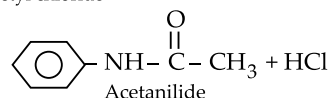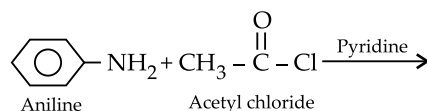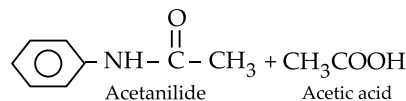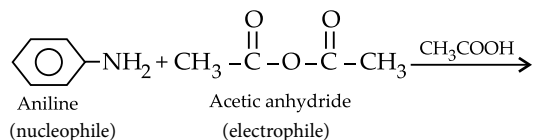
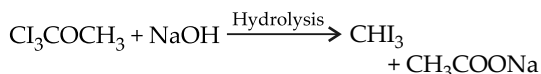❑ *p*-**Nitroacetanilide :** It is prepared by an electrophilic substitution reaction.

Acetanilide (nucleophile) + NO_2^+ (electrophile) $\xrightarrow[< 25°C]{\text{conc. } HNO_3 + \text{conc. } H_2SO_4}$ → p-Nitroacetanilide (Major) + o-Nitroacetanilide (Minor)
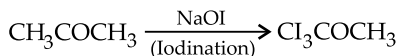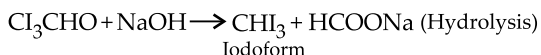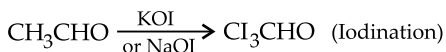
- **Aniline yellow :** It is prepared by coupling benzenediazonium chloride with aniline in acidic medium.

Aniline yellow
(p-Aminoazobenzene)
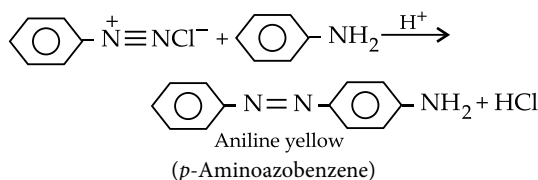
- **Iodoform :** It is prepared by treating organic compound containing $CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-$ or $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-$ with iodine in presence of sodium hydroxide.

$CH_3CH_2OH \xrightarrow[\text{or NaOI}]{KOI} CH_3CHO$ (Oxidation)

$CH_3CHO \xrightarrow[\text{or NaOI}]{KOI} CI_3CHO$ (Iodination)

$CI_3CHO + NaOH \longrightarrow CHI_3 + HCOONa$ (Hydrolysis)
Iodoform

$CH_3COCH_3 \xrightarrow[\text{(Iodination)}]{NaOI} CI_3COCH_3$

$CI_3COCH_3 + NaOH \xrightarrow{\text{Hydrolysis}} CHI_3 + CH_3COONa$
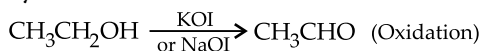
PRACTICAL PHYSICAL CHEMISTRY

- Titrimetric exercises
- Physical chemistry experiments

TIPS TO REMEMBER

TITRIMETRIC EXERCISES

- **Strength of a solution :** It is the amount of solute in grams present per litre of the solution.

- ○ Strength (g/L) = Normality × Eq. wt.
- ○ Strength (g/L) = Molarity × Mol. mass
- **Normality equation :** $N_1V_1 = N_2V_2$
  (Solution 1) (Solution 2)
- **Molarity equation :** $M_1V_1n_1 = M_2V_2n_2$
  (Solution 1) (Solution 2)
  $[\because N = M \times n$, where n = valency factor]
- **Percentage purity of a given salt**

$$= \frac{\text{Strength of pure sample}}{\text{Strength of given sample}} \times 100$$

Types of Titrations

- **Acid-base titrations :** In acid-base titration, the strength of an acid or base is determined by titrating it against a standard solution of base or acid respectively. It involves neutralisation reaction.

$$H^+ + OH^- \longrightarrow H_2O$$
From acid From base Water
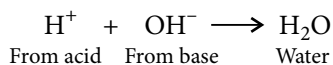
- ○ *Choice of indicators* : The choice of an indicator should be made in such a way that indicator used shows change in colour in the same pH range as developed around the equivalence point.
- ○ *pH range of indicators :*

Indicators	pH range	Colour of indicator	
		Acid medium	Basic medium
Methyl orange	3.1 – 4.4	Red	Orange
Bromo phenol blue	3 – 4.6	Yellow	Blue
Methyl red	4.2 – 6.3	Red	Yellow
Litmus	5 – 8	Red	Blue
Bromo-thymol blue	6 – 7.6	Yellow	Blue
Phenol red	6.8 – 8.4	Yellow	Red
Thymo-phthalein	9.3 – 10.5	Colourless	Blue

Acid	Alkali	Indicator	End point
Strong acid (HCl, H_2SO_4, HNO_3)	Strong alkali (NaOH, KOH)	Phenolphthalein or methyl orange	Pink to colourless or yellow/orange to red, vice versa
Weak acid (oxalic acid, acetic acid)	Strong alkali (NaOH, KOH)	Phenolphthalein	Pink to colourless, vice versa
Strong acid (HCl, H_2SO_4, HNO_3)	Weak alkali (Na_2CO_3, $NaHCO_3$, $KHCO_3$, NH_4OH)	Methyl orange	Yellow/orange to red, vice versa

- ❑ **Redox titrations :** These titrations proceed with transfer of electrons among the reacting ions in aqueous solutions.
  - ○ *Titration of oxalic acid vs* $KMnO_4$
    - – $2KMnO_4 + 3H_2SO_4 + 5\ \underset{COOH}{\overset{COOH}{|}} \cdot 2H_2O$

      $\downarrow$
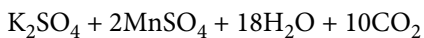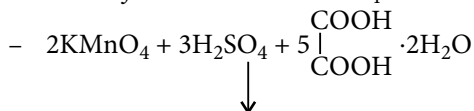
      $K_2SO_4 + 2MnSO_4 + 18H_2O + 10CO_2$
    - – *Calculations*

      $$\frac{M_{KMnO_4} \times V_{KMnO_4}}{M_{oxalic\ acid} \times V_{oxalic\ acid}} = \frac{2}{5}$$
  - ○ *Titration of Mohr's salt vs* $KMnO_4$
    - – $2KMnO_4 + 8H_2SO_4 +$
      $10FeSO_4\cdot(NH_4)_2SO_4\cdot6H_2O \longrightarrow$
      $K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 +$
      $10(NH_4)_2SO_4 + 68H_2O$
    - – *Calculations*
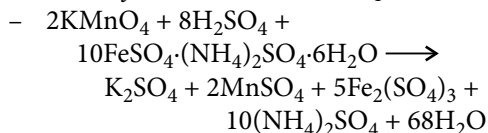
      $$\frac{M_{KMnO_4} \times V_{KMnO_4}}{M_{Mohr's\ salt} \times V_{Mohr's\ salt}} = \frac{1}{5}$$

PHYSICAL CHEMISTRY EXPERIMENTS

- ❑ **Enthalpy of solution of $CuSO_4$**
  - ○ It is the heat change involved during the dissolution of one mole of a solute in such a large excess of solvent so that no further heat change occur on dilution.
    $CuSO_{4(s)} + H_2O \longrightarrow CuSO_{4(aq)}$
  - ○ Dissolution of $CuSO_4$ in water is exothermic. The enthalpy of solution of $CuSO_{4(s)}$ is calculated from the highest temperature attained during its dissolution.
  - ○ *Calculations* : If dissolution of w g of $CuSO_4$ in 200 g solvent (water) causes Δt°C change in temperature, then
    Heat evolved (q) = Mass × Specific heat × Change in temperature

$q = (200 + W) \times 4.2 \times \Delta t$ J, where W is water equivalent of calorimeter (given).
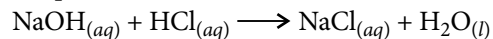Enthalpy of solution of $CuSO_4$ in water

$$= \frac{q \times 159.5 \times 10^{-3}}{w}\ kJ$$

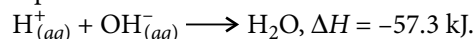$[\because$ Molar mass of $CuSO_4 = 159.5$ g$]$

- ❑ **Enthalpy of neutralisation of strong acid and strong base**
  - ○ It is the enthalpy change accompanying neutralisation of one gram equivalent of a base by an acid in dilute solutions at a given temperature.
    $NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$
    It is an exothermic reaction.
  - ○ The heat of neutralisation of a strong acid by a strong base in their dilute solutions is generally 57.3 kJ. The reaction may be represented as
    $H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O,\ \Delta H = -57.3$ kJ.
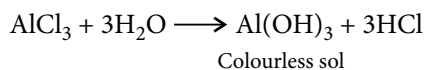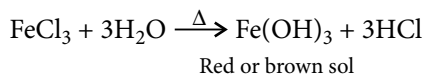 - ○ *Calculations* : Heat evolved during neutralisation of 100 mL of 0.5 N HCl,
    $q = (200 + W) \times \Delta t \times 4.2$ J, where W is water equivalent of calorimeter (given).
    Thus, enthalpy of neutralisation of 1000 mL of 1 N HCl and NaOH $= \dfrac{q}{0.5 \times 100}$ kJ

- ❑ **Preparation of lyophilic sols :** These sols are prepared by shaking the lyophilic material with the dispersion medium. *e.g.* colloidal sols of gelatin, gum, starch, egg albumin, etc.

- ❑ **Preparation of lyophobic sols :** Colloidal sols of ferric hydroxide and aluminium hydroxide can be prepared by hydrolysis of $FeCl_3$ and $AlCl_3$ with boiled distilled water. HCl produced, is removed with dialysis.

$$FeCl_3 + 3H_2O \xrightarrow{\Delta} Fe(OH)_3 + 3HCl$$
<center>Red or brown sol</center>

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$$
<center>Colourless sol</center>

❑ **Kinetic Study of Reaction of Iodide Ion with Hydrogen Peroxide at Room Temperature :** It is based on the principle of set of following three reactions, collectively called clock reaction.

- ○ *Main reaction* : Hydrogen peroxide oxidises iodide ion (from KI) to iodine in acidic medium.

$$H_2O_{2(aq)} + 2I^-_{(aq)} + 2H^+_{(aq)} \xrightarrow{Slow} I_{2(aq)} + 2H_2O_{(l)}$$
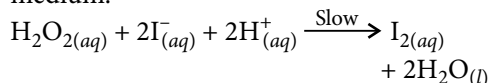
- ○ *Monitor reaction* : When this reaction is carried out in presence of a small amount of sodium thiosulphate and starch, the iodine produced first reacts with sodium thiosulphate as follows :

$$2S_2O_{3(aq)}^{2-} + I_{2(aq)} \xrightarrow{Fast} S_4O_{6(aq)}^{2-} + 2I^-_{(aq)}$$
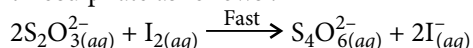
- ○ *Indicator reaction* : When thiosulphate ions get completely consumed, the liberated iodine reacts with starch solution to give blue coloured complex.

$$I_{2(aq)} + starch_{(aq)} \longrightarrow \text{Blue complex}$$
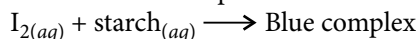
As the concentration of thiosulphate ion is kept constant, the different time taken (t_c) for the appearance of blue colour with change in concentration of either reactant indicates the relative rate of reaction.

$$\text{Initial rate} \propto \frac{1}{t_c}$$

The rate of reaction decreases with decrease in concentration of KI.

The graph of $1/t_c$ versus volume of KI solution is a straight line.
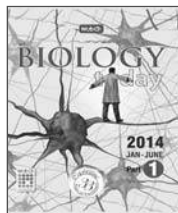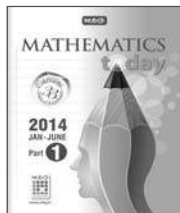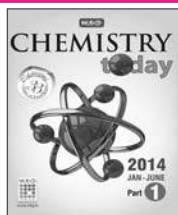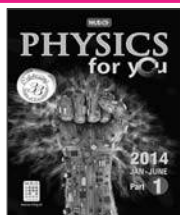

<center>Volume of KI solution (mL)</center>
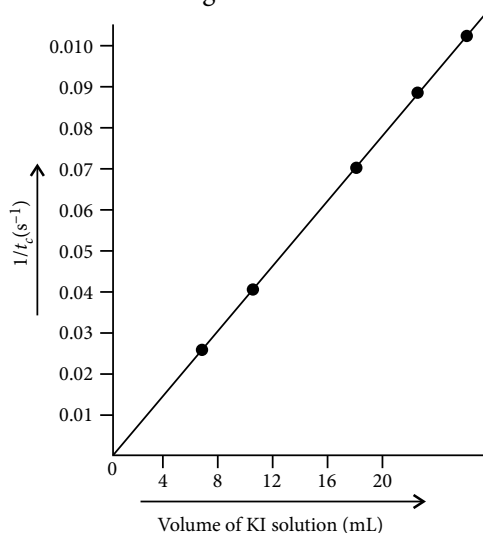
Rate of reaction ∝ Concentration of KI
Similarly, by keeping I^- ion concentration constant and taking different concentrations of H_2O_2, the rate w.r.t. H_2O_2 can be found out.

Exam Café

1. Sodium carbonate cannot be used in place of $(NH_4)_2CO_3$ for the identification of Ca^{2+}, Ba^{2+} and Sr^{2+} ions (in group V) during mixture analysis because
   (a) Mg^{2+} ions will be precipitated
   (b) concentration of CO_3^{2-} ions is very low
   (c) sodium ions will react with acid radicals
   (d) Na^+ ions will interfere with the detection of Ca^{2+}, Ba^{2+}, Sr^{2+} ions.

2. The strength in grams per litre of a solution of sulphuric acid, 12 mL of which neutralise 15 mL of N/10 sodium hydroxide solution is
   (a) 5.302   (b) 6.125
   (c) 6.59   (d) 3.0

3. The compound which gives an oily nitrosamine on reaction with nitrous acid at low temperature is
   (a) CH_3NH_2 (b) $(CH_3)_2CHNH_2$
   (c) $CH_3—NH—CH_3$ (d) $(CH_3)_3N$

4. Which of the following compounds is not expected to show 'Lassaignes' test for nitrogen?
   (a) Propanenitrile
   (b) Hydroxylamine hydrochloride
   (c) Nitromethane
   (d) Ethanamine

5. In the study of oxidation of I^- ions by H_2O_2 in presence of dilute H_2SO_4 as a clock reaction,
   (a) a very small amount of sodium thiosulphate is added so that iodine liberated from main reaction does not react off completely
   (b) a large amount of sodium thiosulphate is added so that iodine liberated from the main reaction reacts off completely
   (c) sodium thiosulphate is added to slow down the reaction
   (d) sodium thiosulphate is added to speed up the reaction.

6. Formation of a rose-red precipitate when a slightly alkaline solution of an inorganic salt is treated with dimethylglyoxime confirms the presence of
   (a) Co^{2+} ions   (b) Zn^{2+} ions
   (c) Fe^{3+} ions   (d) Ni^{2+} ions.

7. Fehling's solution will oxidise

   I. —CHO

   II. —CH—CH$_3$
                              |
                             OH

   III. —CH$_2$CHO

   IV. HCHO
   (a) III and IV   (b) I and IV
   (c) II and IV   (d) all of these.

8. 'X' is a colourless salt giving following reactions:

   White ppt. $\xleftarrow{NaOH}$ X $\xrightarrow{AgNO_3/HNO_3}$
   dissolves in $\downarrow NH_4OH/H_2S$ White ppt.
   excess of NaOH   soluble in
                              White ppt.   aq. NH_3

   'X' can be
   (a) $AlCl_3$ (b) $ZnCl_2$
   (c) $Zn(CH_3COO)_2$ (d) $ZnBr_2$

9. During experiment to calculate heat of neutralisation of strong acid and strong base, temperature should be recorded till
   (a) constant temperature is achieved
   (b) maximum temperature is achieved
   (c) minimum temperature is achieved
   (d) none of these.

10. A salt mixture is heated with dilute HCl and the gaseous product is passed successively through an acidified $K_2Cr_2O_7$ solution and limewater. The colour of the $K_2Cr_2O_7$ solution

changes from orange to green, and the limewater becomes turbid. The salt mixture contains
(a) CO_3^{2-} (b) SO_3^{2-}
(c) S^{2-} (d) CO_3^{2-} as well as SO_3^{2-}

11. The constituents of which of the following pairs of ions in a dilute HCl medium cannot be separated by passing H_2S gas through it?
(a) Ca^{2+} and Hg_2^{2+} (b) Cu^{2+} and Cd^{2+}
(c) Zn^{2+} and Sn^{4+} (d) Co^{2+} and Cu^{2+}

12. Formaldehyde can be distinguished from acetaldehyde by the use of
(a) Schiff's reagent   (b) Tollens' reagent
(c) I_2, Alkali   (d) Fehling's solution.

13. Ferric hydroxide sol can be prepared by shaking
(a) $FeCl_3$ solution with dilute NaOH solution
(b) freshly precipitated $Fe(OH)_3$ with water
(c) freshly precipitated $Fe(OH)_3$ with sufficient amount of dilute HCl
(d) $FeCl_3$ with boiling water.

14. The Lassaigne's extract is boiled with dil. HNO_3 before testing for halogens because
(a) silver halides are soluble in HNO_3
(b) Na_2S and NaCN are decomposed by HNO_3
(c) Ag_2S is soluble in HNO_3
(d) AgCN is soluble in HNO_3.

15. Nitration of aniline is carried out after acylation because
(a) acylation deactivates the $-NH_2$ group
(b) oxidation can be prevented
(c) o- and p-products are obtained in good yield
(d) all of these.

16. In a charcoal cavity test in an oxidizing flame (using cobalt nitrate), salts of aluminium, zinc and magnesium produce residues of specific colour. Which of the following gives the correct match of the composition and colour of the residue?
(a) $CoAl_2O_4 \rightarrow$ Thenard's blue
(b) $CoZnO_2 \rightarrow$ Rinmann's green
(c) $CoMgO_2 \rightarrow$ Pale pink
(d) All of these

17. A carbonyl compound with molecular weight 86, does not reduce Fehling's solution but forms crystalline bisulphite derivative and gives iodoform test. The possible compound can be
(a) 2-pentanone and 3-pentanone
(b) 2-pentanone and 3-methyl-2-butanone
(c) 2-pentanone and pentanal
(d) 3-pentanone and 3-methyl-2-butanone.

18. The purpose of adding dilute sulphuric acid in the preparation of Mohr's salt is to
(a) prevent the hydrolysis of ferrous sulphate
(b) increase the solubility of the salts used
(c) prevent the precipitation of carbonates of metals
(d) neutralise ammonium salts.

19.
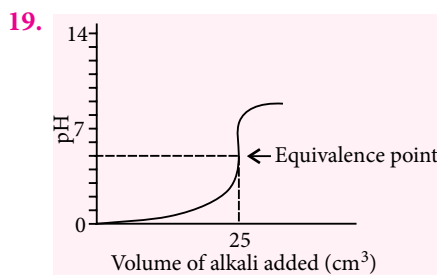
The graph represents titration curve for
(a) strong acid with strong base
(b) weak acid with strong base
(c) strong acid with weak base
(d) weak acid with weak base.

20. Acetaldehyde and acetone can be distinguished by
(a) iodoform test   (b) Molisch test
(c) Fehling's test   (d) none of these.

21. A yellow turbidity, sometimes appears on passing H_2S gas even in the absence of the second group radicals. This happens because
(a) sulphur is present in the mixture as an impurity
(b) the fourth group radicals are precipitated as sulphides
(c) H_2S is oxidised by some acidic radical present in solution
(d) the third group radicals are precipitated.

22. In the green edged flame test for borate, the flame is green only on the edges because
(a) edges represent hottest part of flame where combustion of ethyl borate is complete
(b) it is characteristic property of ethyl borate
(c) ethyl borate vapourises only on the edges
(d) ethyl borate decomposes only on the edges.

23. Xanthate test is meant for
(a) alcohols   (b) phenols
(c) amines   (d) aldehydes.

24. Match the column I with column II and select the correct option.

Column I	Column II
(i) Methanol and ethanol	(p) Lucas reagent
(ii) Phenol and cyclohexanol	(q) Sodium metal
(iii) n-Butyl alcohol and tert-butyl alcohol	(r) Iodoform test
(iv) Methanol and diethyl ether	(s) Ferric chloride

(a) (i)–q, (ii)–s, (iii)–p, (iv)–r
(b) (i)–s, (ii)–p, (iii)–q, (iv)–r
(c) (i)–p, (ii)–q, (iii)–r, (iv)–s
(d) (i)–r, (ii)–s, (iii)–p, (iv)–q

25. In the dry heating test, a white crystalline salt produces crackling noise and also brownish fumes. The residue after heating is seen to be yellow-brown in colour. When a glowing splinter is held in the fumes it is relighted. The fumes consist of
(a) bromine only
(b) nitrogen dioxide only
(c) mixture of O_2 and Br_2
(d) mixture of nitrogen dioxide and oxygen.

26. Azo dye test is used for the detection of
(a) aniline   (b) p-toluidine
(c) phenol   (d) all of these.

27. Positive carbylamine test is shown by
(a) N,N-dimethylaniline
(b) triethylamine
(c) N-methylaniline
(d) p-methylbenzylamine.

28. Identify the correct order of solubility of Na_2S, CuS and ZnS in aqueous medium.
(a) $CuS > ZnS > Na_2S$ (b) $ZnS > Na_2S > CuS$
(c) $Na_2S > CuS > ZnS$ (d) $Na_2S > ZnS > CuS$

29. Mulliken Barker test is meant for
(a) $-\overset{\overset{\displaystyle O}{||}}{C}-NH_2$ group   (b) $-NH_2$ group
(c) $-NH-$ group   (d) $-NO_2$ group.

30. Among the following, the one that gives positive iodoform test upon reaction with I_2 and NaOH is
(a) $CH_3CH_2CH(OH)CH_2CH_3$
(b) $C_6H_5CH_2CH_2OH$
(c) $H_3C-\overset{CH_3}{\underset{OH}{\big\langle}}$
(d) $PhCHOHCH_3$

SOLUTIONS

1. (a) : In group V, $(NH_4)_2CO_3$ is used in the presence of NH_4Cl. In presence of NH_4Cl dissociation of $(NH_4)_2CO_3$ decreases and due to low concentration of CO_3^{2-} ions only V group radicals are precipitated out. If Na_2CO_3 is used, concentration of CO_3^{2-} ions will increase and group VI radical Mg^{2+} ions will also be precipitated.

2. (b) : Applying $N_1V_1 = N_2V_2$
$$\underset{(NaOH)}{}\quad\underset{(H_2SO_4)}{}$$

$$\frac{1}{10}\times 15 = N_2 \times 12$$

$$N_2 = \frac{15}{10\times 12} = 0.125$$

Strength = Normality × Eq. mass
Strength = 0.125 × 49 = 6.125 g/L

3. (c) : Secondary amines on treatment with nitrous acid give oily nitrosamines.

4. (b) : Hydroxylamine hydrochloride does not contain carbon, so in Lassaigne's test it does not result in the formation of NaCN. Hence, it does not give the test of nitrogen, for which formation of NaCN is essential.

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

Elements are classified in such a way that similar elements are grouped together and dissimilar elements are separated from one another.

Earlier Attempts

Döbereiner's Law of Triads
- Elements in a triad had similar properties.
- The atomic weight of the middle element was very close to the arithmetic mean of the other two elements.
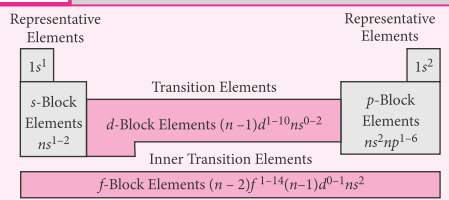
Newland's Law of Octaves
- When elements were arranged in increasing order of their atomic weights, properties of every eighth element were similar to those of the first one like the eighth note of a musical scale.

Mendeleev's Periodic Law
- The properties of the elements are periodic function of their atomic weights.
- Mendeleev's original periodic table contains 8 vertical columns called *groups* and 6 horizontal rows called *periods*.

Blocks

Representative Elements $1s^1$

Representative Elements $1s^2$

Transition Elements

s-Block Elements ns^{1-2}

d-Block Elements $(n-1)d^{1-10}ns^{0-2}$

p-Block Elements ns^2np^{1-6}

Inner Transition Elements

f-Block Elements $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

Arrangement of Elements
- **Metals :** > 78% of all known elements appear on the left hand side of the periodic table.
- **Non metals :** < 20, lie on the top right hand side of the periodic table.
- **Metalloids or semi-metals :** B, Si, Ge, As, Sb, Te, Po and At, run diagonally across the periodic table.

Modern Periodic Table

Modern Periodic Law
- The physical and chemical properties of the elements are a periodic function of their atomic numbers.

Long Form of Periodic Table
- Based on modern periodic law.
- Follows Bohr's scheme for the arrangement of various electrons around the nucleus.
- Contains 18 groups and 7 periods.

Groups
- **Group number for**
  - s-block : no. of valence electrons in ns-orbital.
  - p-block : 10 + no. of valence electrons in np-orbital.
  - d-block : no. of valence electrons in $(n-1)d$ and ns-orbitals.
- Group 1 - Alkali metals
- Group 2 - Alkaline earth metals
- Group 11 - Coinage metals
- Group 15 - Pnictogens
- Group 16 - Chalcogens
- Group 17 - Halogens
- Group 18 - Noble gases or Aerogens.

Periods
- **Periodic number :** highest principal quantum number (n) of the elements of the periodic table.
- Number of elements in each period is twice of the atomic orbitals available in the energy level that are being filled.
- Period 1 ($n = 1$) - 2 elements
- Period 2 ($n = 2$) - 8 elements
- Period 3 ($n = 3$) - 8 elements
- Period 4 ($n = 4$) - 18 elements
- Period 5 ($n = 5$) - 18 elements
- Period 6 ($n = 6$) - 32 elements
- Period 7 ($n = 7$) - 32 elements
  - **Lanthanoids :** 14 elements of period 6
  - **Actinoids :** 14 elements of period 7

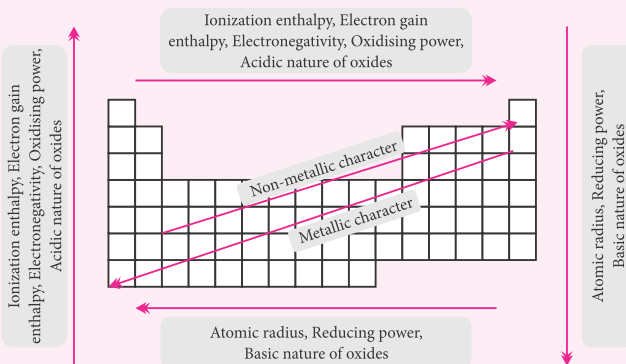(Placed in the bottom of the periodic table separately.)

Periodic Trends

Periodic Properties
- Properties which show a regular gradation from left to right in a period and top to bottom in a group.

Exceptions
- $\Delta_{eg}H$ of Be, Mg, Ca, N and inert gases is positive.
- Ar and Kr have the same value of $\Delta_{eg}H$.
- $\Delta_{eg}H$ of F is less –ve than Cl.
- $\Delta_{eg}H$ of O is less –ve than S.
- $I.E._1$ of O $< I.E._1$ of N.

Properties

Ionization enthalpy, Electron gain enthalpy, Electronegativity, Oxidising power, Acidic nature of oxides

Ionization enthalpy, Electron gain enthalpy, Electronegativity, Oxidising power, Acidic nature of oxides

Non-metallic character

Metallic character

Atomic radius, Reducing power, Basic nature of oxides
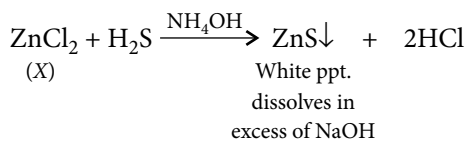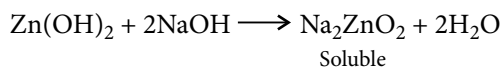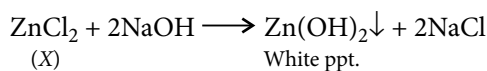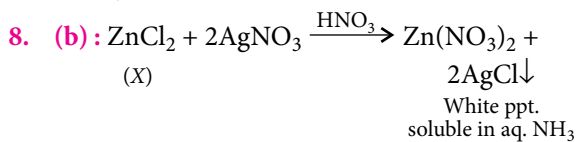
Atomic radius, Reducing power, Basic nature of oxides

Have a Look!
- ☞ Mendeleev had predicted the properties of gallium (*eka-aluminium*) and germanium (*eka-silicon*) long before they were known.
- ☞ IUPAC names of elements with atomic numbers > 100 are derived directly from the atomic numbers using numerical roots for 0 and number from 1 – 9 and adding suffix *ium*.
- ☞ Valency first increases from 1 to 4 and then decreases to zero along a period and remains same within a group.
- ☞ Some elements in second period show similarities with third period elements placed diagonally to each other.
- ☞ Boron (B) has the smallest atomic volume and highest tensile strength.
- ☞ Technetium (Tc) is the first synthetic element.
- ☞ Lanthanide which does not occur in nature is promethium (Pm).
- ☞ Francium (Fr) is liquid, radioactive element.
- ☞ Zn, Cd and Hg are volatile *d*-block elements.
- ☞ Mercury (Hg) is also called 'liquid silver'.

5. (a) : A small amount of sodium thiosulphate is added so that iodine liberated from main reaction does not react off completely and gives blue colour with starch.
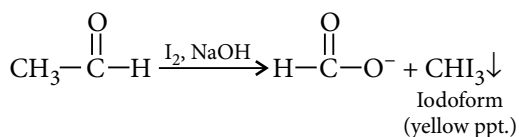
6. (d) : Rose-red ppt. is due to $[Ni(dmg)_2]$ complex.

7. (a) : Fehling's solution oxidises only aliphatic aldehydes.

8. (b) : $ZnCl_2 + 2AgNO_3 \xrightarrow{HNO_3} Zn(NO_3)_2 +$
$\quad\;\;$ (*X*) $\qquad\qquad\qquad\qquad 2AgCl\downarrow$
$\qquad\qquad\qquad\qquad\qquad\quad$ White ppt.
$\qquad\qquad\qquad\qquad\;\;$ soluble in aq. NH_3

$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2\downarrow + 2NaCl$
$\;$ (*X*) $\qquad\qquad\qquad$ White ppt.

$Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$
$\qquad\qquad\qquad\qquad\qquad$ Soluble

$ZnCl_2 + H_2S \xrightarrow{NH_4OH} ZnS\downarrow + 2HCl$
$\;$ (*X*) $\qquad\qquad\qquad$ White ppt.
$\qquad\qquad\qquad\qquad$ dissolves in
$\qquad\qquad\qquad\quad$ excess of NaOH

9. (a) $\qquad$ **10. (d)** $\qquad$ **11. (b)**

12. (c) : Acetaldehyde gives iodoform test.

$$CH_3\!-\!\overset{\overset{\displaystyle O}{||}}{C}\!-\!H \xrightarrow{I_2,\,NaOH} H\!-\!\overset{\overset{\displaystyle O}{||}}{C}\!-\!O^- + CHI_3\downarrow$$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ Iodoform
$\qquad\qquad\qquad\qquad\qquad\qquad\quad$ (yellow ppt.)

Formaldehyde does not form iodoform.

13. (d) : $Fe(OH)_3$ sol is prepared by shaking $FeCl_3$ with boiling water.

14. (b) : Na_2S and $NaCN$, formed during fusion with metallic sodium, must be removed before adding $AgNO_3$, otherwise black ppt. due to Ag_2S or white precipitate due to AgCN will be formed and thus white precipitate of AgCl will not be identified easily.

15. (d) $\qquad$ **16. (d)** $\qquad$ **17. (b)**

18. (a) : $FeSO_4$ undergoes hydrolysis to produce $Fe(OH)_2$ and H_2SO_4.
$FeSO_4 + 2H_2O \rightarrow Fe(OH)_2 + H_2SO_4$
To prevent hydrolysis, dil. H_2SO_4 is added in the preparation of Mohr's salt.
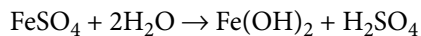
19. (c) : Since at equivalence point pH is less than 7 it must be the titration curve of strong acid with weak base.

20. (c) : Acetaldehyde is easily oxidised to acetic acid by a mild oxidising agent like Fehling's solution. Acetone is not easily oxidised.
Both acetone and acetaldehyde give iodoform test. Other two conditions are not relevant to aldehydes and ketones.

21. (c) : Radicals such as NO_3^- oxidise H_2S to S which appears as yellow turbidity.

22. (a)

23. (a) : When little of alcohol is warmed with a pellet of KOH, it dissolves. After cooling, add a few drops of CS_2 and shake. Yellow ppt. of xanthate indicates an alcoholic (—OH) group.

24. (d)

25. (d) : The data indicates the presence of $Pb(NO_3)_2$, which decomposes on heating to give gases NO_2 and O_2.

$$Pb(NO_3)_2 \xrightarrow{\Delta} PbO + 2NO_2 + \frac{1}{2}O_2$$
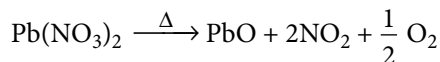
**26. (d) :** This test is given both by phenols and amines.

27. (d) : Only primary amines give carbylamine test.

28. (d) : Na_2S is strongly electrovalent. Copper belongs to group II and precipitates first as CuS (black) whereas zinc belongs to group IV and precipitates later as ZnS (greenish white), hence solubility order is $Na_2S > ZnS > CuS$.

29. (d) : Mulliken Barker test is for —NO_2 group.

30. (d) : Iodoform test is given by only the compounds containing CH_3CO— or $CH_3CH(OH)$— group.

$PhCHOHCH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta}$
$\qquad\qquad CHI_3 + PhCOONa + 5NaI + 5H_2O$

■■
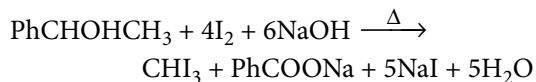
1. A certain metal when irradiated by light ($\upsilon = 3.2 \times 10^{16}$ Hz) emits photoelectrons with twice *K.E.* as did photoelectrons when the same metal is irradiated by light ($\upsilon = 2.0 \times 10^{16}$ Hz). The υ_0 of the metal is
   (a) 1.2×10^{14} Hz   (b) 8×10^{15} Hz
   (c) 1.2×10^{16} Hz   (d) 4×10^{12} Hz

2. Identify *X* and *Y* in the reaction.

   $$CH_3-CH-CONH_2 \xrightarrow{Br_2/NaOH} X \xrightarrow{HNO_2} Y$$
   $$\overset{|}{CH_3}$$

X	**Y**

   (a) $CH_3-\overset{\overset{\displaystyle |}{CH_3}}{CH}-CH_2NH_2$; $CH_3-\overset{\overset{\displaystyle |}{CH_3}}{CH}-CH_2OH$

   (b) $CH_3CH=CHNH_2$; $CH_3CH=CHOH$

   (c) $CH_3-\overset{\overset{\displaystyle |}{CH_3}}{CH}-NH_2$; $CH_3-\overset{\overset{\displaystyle |}{CH_3}}{CH}-OH$

   (d) $CH_3CH_2CH_2NH_2$; $CH_3CH_2CH_2OH$

3. If the concentration of glucose ($C_6H_{12}O_6$) in blood is 0.9 g L^{-1}, what will be the molarity of glucose in blood?
   (a) 5 M   (b) 50 M
   (c) 0.005 M   (d) 0.5 M

4. When sodium peroxide is treated with dilute sulphuric acid, we get
   (a) sodium sulphate and water
   (b) sodium sulphate and oxygen
   (c) sodium sulphate, hydrogen and oxygen
   (d) sodium sulphate and hydrogen peroxide.

5. In a vessel N_2, H_2 and NH_3 are at equilibrium. Some helium gas is introduced into the vessel so that total pressure increases while temperature and volume remain constant. According to Le Chatelier's principle, the dissociation of NH_3
   (a) increases
   (b) decreases
   (c) remains unchanged
   (d) equilibrium is disturbed.

6. Which of the following statements is correct according to the basic concepts of thermodynamics which govern the feasibility of a metallurgical process?
   (a) When the value of ΔG is positive for the equation $\Delta G = \Delta H - T\Delta S$, the reaction will proceed.
   (b) If reactants and products of two reactions are put together and net ΔG is –ve, the overall reaction will occur.
   (c) On increasing the temperature, the value of ΔG becomes +ve.
   (d) Feasibility of thermal reduction of an ore can be established by Ellingham diagram in which a straight line shows the reaction will proceed.

7. Which of the following compounds will react with Na to form 4,5-diethyloctane?
   (a) $CH_3CH_2CH_2CH_2Br$
   (b) $CH_3CH_2CH_2-\overset{\overset{\displaystyle |}{CH_3}}{CH}-CH_2CH_2Br$

(c) $CH_3CH_2CH_2CH_2$—CH—CH_3
            |
            Br

(d) $CH_3CH_2CH_2$—CH—CH_2CH_3
            |
            Br
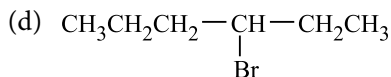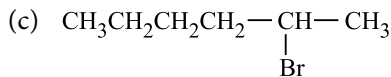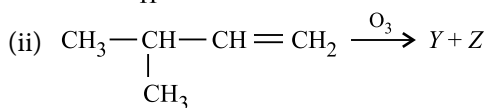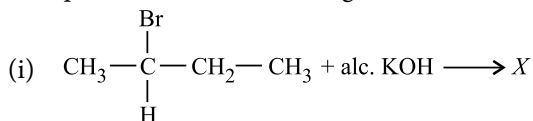
8. An alcohol X when treated with hot conc. H_2SO_4 gave an alkene Y with formula C_4H_8. This alkene on ozonolysis gives single product with molecular formula C_2H_4O. The alcohol is
   (a) butan-1-ol
   (b) butan-2-ol
   (c) 2-methylpropan-1-ol
   (d) 2,2-dimethylbutan-1-ol.

9. The potential energy diagram for a reaction $X \rightarrow Y$ is given. A and C in the graph correspond to
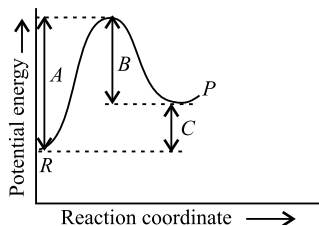
   (a) $A \rightarrow$ activation energy, $C \rightarrow \Delta H°$
   (b) $A \rightarrow$ energy of reactants, $C \rightarrow$ energy of products
   (c) $A \rightarrow \Delta H°$, $C \rightarrow$ activation energy
   (d) $A \rightarrow$ activation energy, $C \rightarrow$ threshold energy

10. A gas that follows Boyle's law, Charles' law and Avogadro's law is called an ideal gas. Under what conditions a real gas behaves as ideal gas?
    (a) Under low pressure and temperature.
    (b) Under high pressure and temperature.
    (c) Under high pressure and low temperature.
    (d) Under low pressure and high temperature.

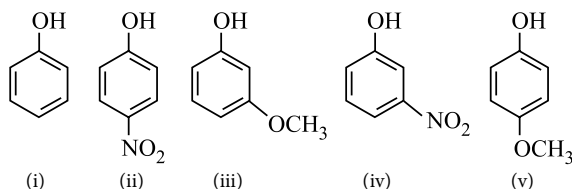11. The products for the following reactions are

(i)   Br
        |
    CH_3—C—CH_2—CH_3 + alc. KOH $\longrightarrow X$
        |
        H

(ii) CH_3—CH—CH=CH_2 $\xrightarrow{O_3}$ $Y + Z$
        |
        CH_3

(a) $X = (CH_3)_2C=CH_2$, $Y = CH_3CH_2CHO$,
    $Z = CH_3CH_2CHO$
(b) $X = CH_2=CH_2$, $Y = CH_3CHO$,
    $Z = CH_3COOH$
(c) $X = CH_3$—CH=CHCH_3,
                    CH_3
                    |
    $Y = CH_3$—CH—CHO, $Z =$ HCHO
(d) $X = CH_3$—CH=C(CH_3)_2, $Y =$ HCHO,
    $Z = CH_3CHO$
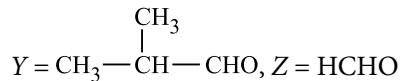
12. Mark the correct order of decreasing acid strength of the following compounds.

(i)   (ii)   (iii)   (iv)   (v)

    (a) (v) > (iv) > (ii) > (i) > (iii)
    (b) (ii) > (iv) > (i) > (iii) > (v)
    (c) (iv) > (v) > (iii) > (ii) > (i)
    (d) (v) > (iv) > (iii) > (ii) > (i)

13. A compound is formed by two elements Y and Z. The element Z forms *ccp* and atoms Y occupy 1/3 rd of tetrahedral voids. The formula of the compound is
    (a) Y_2Z_3 (b) YZ
    (c) YZ_3 (d) Y_2Z

14. Match the column I with column II and mark the appropriate choice.

Column I		Column II	
(A)	H_2SO_3	(i)	+6, dibasic
(B)	H_2SO_5	(ii)	+5, dibasic
(C)	$H_2S_2O_6$	(iii)	+6, monobasic
(D)	H_2SO_4	(iv)	+4, dibasic

(a) (A) $\rightarrow$ (i); (B) $\rightarrow$ (ii); (C) $\rightarrow$ (iii); (D) $\rightarrow$ (iv)
(b) (A) $\rightarrow$ (ii); (B) $\rightarrow$ (iii); (C) $\rightarrow$ (i); (D) $\rightarrow$ (iv)
(c) (A) $\rightarrow$ (iii); (B) $\rightarrow$ (iv); (C) $\rightarrow$ (ii); (D) $\rightarrow$ (i)
(d) (A) $\rightarrow$ (iv); (B) $\rightarrow$ (iii); (C) $\rightarrow$ (ii); (D) $\rightarrow$ (i)

15. What is the order of stability of N_2 and its ions?

(a) $N_2 > N_2^+ = N_2^- > N_2^{2-}$

(b) $N_2^+ > N_2^- > N_2 > N_2^{2-}$

(c) $N_2^- > N_2^+ > N_2 > N_2^{2-}$

(d) $N_2^{2-} > N_2^- = N_2^+ > N_2$

16. Complete the following reactions by filling the appropriate choice.

$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + \underline{(i)} + \underline{(ii)}$

$XeF_6 + 3H_2O \rightarrow \underline{(iii)} + 6HF$

	(i)	(ii)	(iii)
(a)	F_2	H_2O	$XeOF_4$
(b)	24HF	$3O_2$	XeO_3
(c)	2HF	$2H_2O$	XeO
(d)	HF	H_2O	Xe_2O_3

17. For the cell reaction : $2Cu^+_{(aq)} \rightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$, the standard cell potential is 0.36 V. The equilibrium constant for the reaction is

(a) 1.2×10^6 (b) 7.4×10^{12}

(c) 2.4×10^6 (d) 5.5×10^8

18. Silica is added to the sulphide ore of copper in reverberatory furnace because

(a) sulphide ore of copper contains iron as impurity which is removed as iron slag

(b) silica reacts with Cu_2O to form slag

(c) silica helps in reduction of Cu_2O to Cu

(d) sulphide ore of copper is separated from iron by reacting with silica.

19. The number of radial nodes and angular nodes for d-orbital can be represented as

(a) $(n-2)$ radial nodes + 1 angular node $= (n-1)$ total nodes

(b) $(n-1)$ radial nodes + 1 angular node $= (n-1)$ total nodes

(c) $(n-3)$ radial nodes + 2 angular nodes $= (n-l-1)$ total nodes

(d) $(n-3)$ radial nodes + 2 angular nodes $= (n-l)$ total nodes.

20. The first ionization enthalpies of Na, Mg, Al and Si are in the order

(a) Na < Mg > Al < Si

(b) Na > Mg > Al > Si

(c) Na < Mg < Al < Si

(d) Na > Mg > Al < Si

21. The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$?

(a) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

(b) $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$

(c) $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$

(d) $[Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-} > [Co(H_2O)_6]^{3+}$

22. To differentiate between pentan-2-one and pentan-3-one a test is carried out. Which of the following is the correct answer?

(a) Pentan-2-one will give silver mirror test

(b) Pentan-2-one will give iodoform test.

(c) Pentan-3-one will give iodoform test

(d) None of these.

23. On the basis of thermochemical equations (i), (ii) and (iii), find out which of the algebric relationships given in options (a) to (d) is correct.

(i) $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta_r H = x$ kJ mol^{-1}

(ii) $C_{(graphite)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)}$; $\Delta_r H = y$ kJ mol^{-1}

(iii) $CO_{(g)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta_r H = z$ kJ mol^{-1}

(a) $z = x + y$ (b) $x = y - z$

(c) $x = y + z$ (d) $y = 2z - x$

24. Complete the following reactions.

(i) $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 2Cr^{3+} + \underline{\quad} + H_2O$

(ii) $2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + \underline{\quad} + 3H_2O$

(iii) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + \underline{\quad} + 7H_2O$

(a) $3SO_4^{2-}$, SO_2, Fe^{3+}

(b) $3SO_4^{2-}$, $5SO_4^{2-}$, $6Fe^{3+}$

(c) $3SO_4^{2-}$, SO_2, K^+

(d) S, SO_2, Fe^{3+}

25. Which of the following is a tetrabasic acid?

(a) Hypophosphorous acid

(b) Metaphosphoric acid
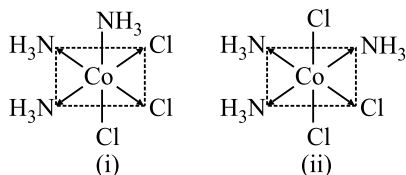
(c) Pyrophosphoric acid

(d) Orthophosphoric acid

26. An organic compound with molecular formula $C_4H_{10}O$ does not react with sodium. With excess of HI it gives only one type of alkyl halide. The compound is

(a) $C_2H_5OC_2H_5$
(b) CH_3CHCH_3
     $\quad\quad |$
     $\quad\quad OCH_3$
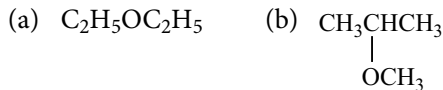
(c) $CH_3CH_2CH_2OCH_3$
(d) $CH_3CH_2CH_2CH_2OH$

27. Two isomers of a compound $Co(NH_3)_3Cl_3$ (MA_3B_3 type) are shown in the figures.


    (i)   (ii)

The isomers can be classified as

(a) (i) *fac*-isomers (ii) *mer*-isomer
(b) (i) optical-isomer (ii) *trans*-isomer
(c) (i) *mer*-isomer (ii) *fac*-isomer
(d) (i) *trans*-isomer (ii) *cis*-isomer.

28. In nucleophilic addition reactions, the reactivity of carbonyl compounds follows the order

(a) $HCHO > RCHO > ArCHO > R_2CO > Ar_2CO$
(b) $HCHO > R_2CO > Ar_2CO > RCHO > ArCHO$
(c) $Ar_2CO > R_2CO > ArCHO > RCHO > HCHO$
(d) $ArCHO > Ar_2CO > RCHO > R_2CO > HCHO$

29. A certain compound X imparts a golden yellow flame. When zinc powder is heated with concentrated solution of X, H_2 gas is evolved. X combines with CO_2 to give a salt Y. Y is a hydrated salt which on reaction with HCl or excess of CO_2 gives another salt Z which is an important part of baking powder. Identify X, Y and Z.

	X	Y	Z
(a)	NaOH	Na_2CO_3	$NaHCO_3$
(b)	HCl	NaOH	$NaHCO_3$
(c)	KOH	K_2CO_3	$KHCO_3$
(d)	NaCl	Na_2CO_3	NaOH

30. α-Hydroxypropanoic acid can be prepared from ethanal by

(a) treating with HCN followed by acidic hydrolysis

(b) treating with $NaHSO_3$ followed by reaction with Na_2CO_3

(c) treating with H_2SO_4 followed by hydrolysis

(d) treating with $K_2Cr_2O_7$ in presence of sulphuric acid.

31. What are X and Y in the reaction?

$$3B_2H_6 + 6X \longrightarrow 3[BH_2(X)_2]^+[BH_4]^-$$
$$\xrightarrow{\text{heat}} Y + 12H_2$$
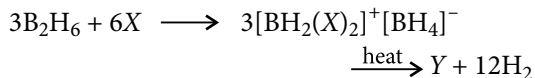
(a) $X = NH_3, Y = B_3N_3H_6$
(b) $X = CO, Y = BH_3CO$
(c) $X = NaH, Y = NaF$
(d) $X = NF_3, Y = B_3N_3$

32. Consider the following bromides :

  (A)   (B)   (C)
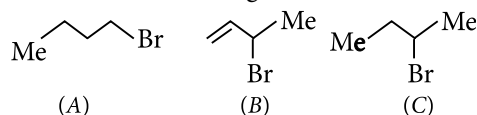
The correct order of S_N1 reactivity is

(a) $A > B > C$ (b) $B > C > A$
(c) $B > A > C$ (d) $C > B > A$

33. Identify the incorrect statement among the following.

(a) $4f$ and $5f$ orbitals are equally shielded.
(b) d-Block elements show irregular and erratic chemical properties among themselves.
(c) La and Lu have partially filled d-orbitals and no other partially filled orbitals.
(d) The chemistry of various lanthanoids is very similar.

34. Which of the following ores is concentrated by chemical leaching method?

(a) Cinnabar   (b) Argentite
(c) Copper pyrites   (d) Galena

35. The property of halogens which is not correctly matched is

(a) $F > Cl > Br > I$ (Ionisation energy)
(b) $F > Cl > Br > I$ (Electronegativity)
(c) $I > Br > Cl > F$ (Density)
(d) $F > Cl > Br > I$ (Electron affinity)

36. The equivalent conductance of Ba^{2+} and Cl^- are respectively 127 and 76 $ohm^{-1}cm^2\,eq^{-1}$ at infinite dilution. What will be the equivalent conductance of $BaCl_2$ at infinite dilution?

(a) 139.5 ohm^{-1} cm^2 eq^{-1}

(b) 203 ohm^{-1} cm^2 eq^{-1}

(c) 279 ohm^{-1} cm^2 eq^{-1}

(d) 101.5 ohm^{-1} cm^2 eq^{-1}

37. The distance between Na$^+$ and Cl$^-$ ions in NaCl with a density 2.165 g cm^{-3} is
(a) 564 pm (b) 282 pm
(c) 234 pm (d) 538 pm

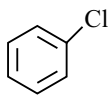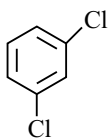38. One word answers are given for the following. Mark the example which is not correct.
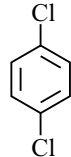(a) Alkali metal with lowest melting point - Cs
(b) Alkaline earth metal with highest hydration enthalpy - Ba^{2+}
(c) Alkaline earth metal which imparts brick red colour to the flame - Ca^{2+}
(d) Oxide of alkaline earth metal which is amphoteric in nature - BeO

39. The members of group 14 form tetrahalides of the type MX_4. Which of the following halides cannot be readily hydrolysed by water?
(a) CX_4 (b) SiX_4
(c) GeX_4 (d) SnX_4

40. Identify the compound 'Y' in the following reaction.
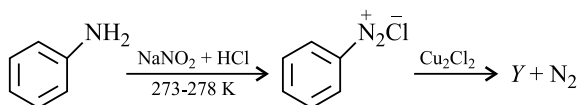
(a)   (b)

(c)   (d)

41. The types of hybrid orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are expected to be
(a) sp, sp^3 and sp^2 (b) sp, sp^2 and sp^3
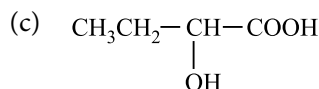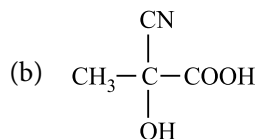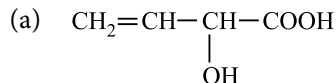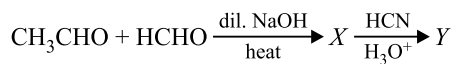(c) sp^2, sp and sp^3 (d) sp^2, sp^3 and sp

42. Using the standard electrode potential, find out the pair between which redox reaction is not feasible.

$E°$ values : Fe^{3+}/Fe^{2+} = + 0.77; I$_2$/I$^-$ = + 0.54; Cu^{2+}/Cu = + 0.34; Ag$^+$/Ag = + 0.80 V
(a) Fe^{3+} and I$^-$ (b) Ag$^+$ and Cu
(c) Fe^{3+} and Cu (d) Ag and Fe^{3+}

43. Study the following sequence of reactions and identify the product (Y).

$$CH_3CHO + HCHO \xrightarrow[\text{heat}]{\text{dil. NaOH}} X \xrightarrow[\text{H}_3\text{O}^+]{\text{HCN}} Y$$

(a)

(b)

(c)

(d)
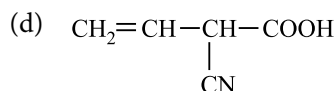
44. Dinitrogen and dioxygen are main constituents of air, but these do not react with each other to form oxides of nitrogen because
(a) the reaction is endothermic and requires very high temperature
(b) the reaction can be initiated only in presence of a catalyst
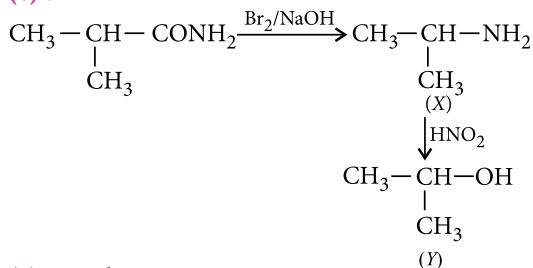(c) oxides of nitrogen are unstable
(d) N$_2$ and O$_2$ are unreactive

45. What is tincture of iodine?
(a) 2-3% solution of iodine in alcohol-water mixture.
(b) A mixture of iodine in chloroxylenol.
(c) A mixture of 0.2% phenol and 2-3% iodine in water.
(d) 2-3% solution of iodine in potassium iodide.

SOLUTIONS

1. **(b)**: $(K.E.)_1 = h\upsilon_1 - h\upsilon_0$
   $(K.E.)_2 = h\upsilon_2 - h\upsilon_0$
   As $(K.E.)_1 = 2 \times (K.E.)_2$
   $\therefore$ $(h\upsilon_1 - h\upsilon_0) = 2(h\upsilon_2 - h\upsilon_0)$
   or $\upsilon_0 = 2\upsilon_2 - \upsilon_1 = 2 \times (2 \times 10^{16}) - (3.2 \times 10^{16})$
   $= 0.8 \times 10^{16}$ Hz or 8×10^{15} Hz

2. (c) :

$$CH_3-CH-CONH_2 \xrightarrow{Br_2/NaOH} CH_3-CH-NH_2$$

with CH_3 group below first carbon, and CH_3 below second (X)

$$\downarrow HNO_2$$

$$CH_3-CH-OH$$
$$\underset{(Y)}{\overset{|}{CH_3}}$$

3. (c) : Molarity

$$= \frac{W_B \text{ (in g)}}{M_B \text{ (in g mol}^{-1}) \times \text{Volume of solution (in L)}}$$

$$= \frac{\text{Conc. (in g L}^{-1})}{M_B \text{ (in g mol}^{-1})} = \frac{0.9}{180} = 0.005 \text{ M}$$

($\because$ Molar mass of $C_6H_{12}O_6$ = 180 g mol^{-1})

4. (d) : $\underset{\substack{\text{Sodium} \\ \text{peroxide}}}{Na_2O_2} + H_2SO_{4(dil.)} \rightarrow \underset{\substack{\text{Sodium} \\ \text{sulphate}}}{Na_2SO_4} + \underset{\substack{\text{Hydrogen} \\ \text{peroxide}}}{H_2O_2}$

5. (c) : Addition of inert gas at constant volume does not affect the equilibrium as there is no change in partial pressures of reactants and products.

6. (b) : The process of interpretation involves coupling of two reactions, getting the sum of ΔG and looking for its sign. Overall –ve value of ΔG shows that reduction of ore is possible.

7. (d) : The reaction is Wurtz reaction and proceeds as follows :

$$CH_3CH_2CH_2-CH-Br + 2Na +$$
$$\overset{|}{CH_2CH_3}$$

$$Br-CH-CH_2CH_2CH_3 \xrightarrow{ether}$$
$$\overset{|}{CH_2CH_3}$$

$$\overset{8}{C}H_3\overset{7}{C}H_2\overset{6}{C}H_2-\overset{5}{C}H-\overset{4}{C}H-\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_3$$
$$\qquad\quad \overset{|}{CH_3CH_2} \ \overset{|}{CH_2CH_3}$$
4,5-Diethyloctane

8. (b) :

$$\underset{\substack{OH \\ (X) \\ \text{Butan-2-ol}}}{CH_3-CHCH_2CH_3} \xrightarrow[\Delta]{conc. H_2SO_4} \underset{Y\ (C_4H_8)}{CH_3CH=CHCH_3}$$

$$\downarrow \text{Ozonolysis}$$
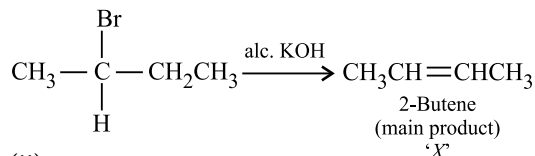
$$\underset{(C_2H_4O)}{2CH_3CHO}$$
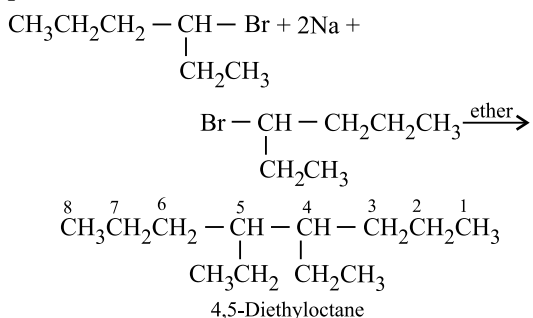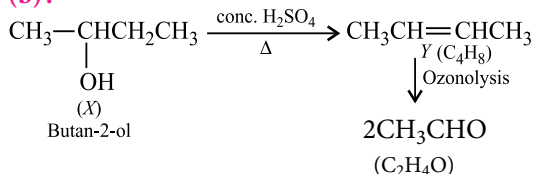
9. (a) : $\Delta H°$ is the difference in energy of reactants and products.
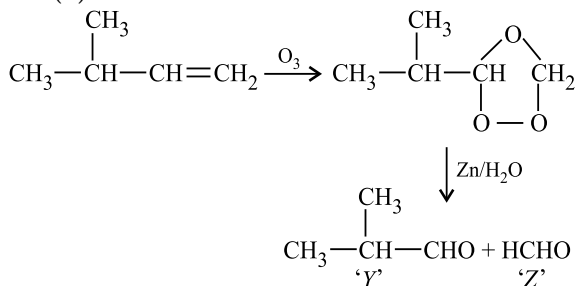
10. (d) : Under low pressure and high temperature two postulates of kinetic theory of gases become true.
(i) Volume of the particles of gas is negligible as compared to the volume of the gas occupied.
(ii) There is no force of attraction between the molecules of a gas.

11. (c) : (i)

$$CH_3-\overset{\overset{Br}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CH_3 \xrightarrow{alc.\ KOH} \underset{\substack{\text{2-Butene} \\ \text{(main product)} \\ 'X'}}{CH_3CH=CHCH_3}$$

(ii)

$$\underset{\overset{|}{CH_3}}{CH_3-CH}-CH=CH_2 \xrightarrow{O_3} CH_3-\underset{\overset{|}{CH_3}}{CH}-\underset{\substack{| \ \ \ | \\ O-O}}{CH \ \ CH_2}^{O}$$

$$\downarrow Zn/H_2O$$

$$\underset{'Y'}{CH_3-\underset{\overset{|}{CH_3}}{CH}-CHO} + \underset{'Z'}{HCHO}$$

12. (b) : The electron withdrawing group ($-NO_2$) increases the acidity of phenols and the electron donating group ($-OCH_3$) decreases the acidity of phenols. The effect at p-position is greater than at m-position.

13. (a) : Suppose no. of atoms of $Z = a$
No. of tetrahedral voids = $2a$
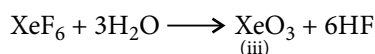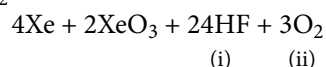
No. of atoms of $Y = \frac{1}{3} \times 2a = \frac{2a}{3}$

Ratio of atoms of Y and $Z = \frac{2a}{3} : a = 2 : 3$

Hence, the formula of the compound = Y_2Z_3

14. (d)

15. (a) : Bond order of $N_2 = 3, N_2^+ = 2.5, N_2^- = 2.5$ and N_2^{2-} is 2. Higher the bond order, more is the stability.

16. (b) : $\underset{(i)}{6XeF_4} + 12H_2O \longrightarrow$
$$\underset{(i)\qquad\quad (ii)}{4Xe + 2XeO_3 + 24HF + 3O_2}$$

$$\underset{(iii)}{XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF}$$

17. (a) : $\log K_c = \frac{nE°_{cell}}{0.0591}$

For the given reaction, $n = 1$

$$\log K_c = \frac{1 \times 0.36}{0.0591} = 6.09$$

K_c = antilog $6.09 = 1.2 \times 10^6$

18. (a)

19. (d): Total number of nodes = $n - 1$

For d-orbital, radial nodes = $n - 3$ and there are 2 angular nodes.

Number of spherical nodes in any orbital is given by $n - l - 1$ and the number of angular nodes is given by l. i.e., for p, 1 angular node; for d, 2 angular nodes and so on.

20. (a): As we move across the period, atomic size decreases, hence, ionization enthalpy increases. But for Al ($3s^2 3p^1$), electron has to be removed from outer $3p$ orbital whereas in Mg($3s^2$), electron has to be removed from stable fully filled $3s$ orbital. Thus, I.E. for Mg > Al. So, the correct order of first ionization enthalpies is Na < Mg > Al < Si.

21. (c): The CFSE of the ligands is in the order :

$$H_2O < NH_3 < CN^-$$

Hence, excitation energies are in the order:

$$[Co(H_2O)_6]^{3+} < [Co(NH_3)_6]^{3+} < [Co(CN)_6]^{3-}$$
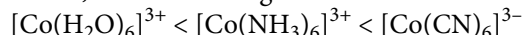
From the relation $E = \dfrac{hc}{\lambda} \Rightarrow E \propto \dfrac{1}{\lambda}$

The order of absorption of wavelength of light in the visible region is

$$[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$$
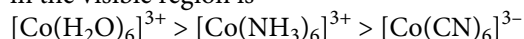
22. (b): Pentan-2-one will give positive iodoform test while pentan-3-one will not give this test.

$$CH_3COCH_2CH_2CH_3 + I_2 + NaOH \longrightarrow CHI_3$$
$$\text{(Iodoform)}$$
$$+ \text{ other products}$$

23. (c): $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)};$

$$\Delta_r H = x \text{ kJ mol}^{-1} \quad ..(i)$$

$$C_{(graphite)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}; \Delta_r H = y \text{ kJ mol}^{-1} \quad ...(ii)$$
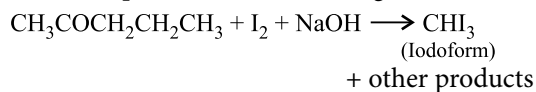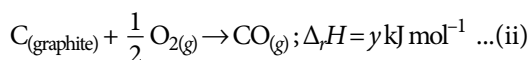
By substracting eqn (ii) from (i), we get

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}; \Delta_r H = z \text{ kJ mol}^{-1} \quad ...(iii)$$
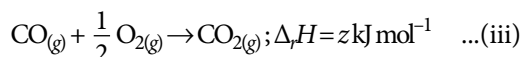
Thus, $x - y = z$ i.e., $x = y + z$

24. (b)

25. (c)

26. (a): $C_4H_{10}O$ can have two structures :

$CH_3CH_2CH_2CH_2OH$ and $C_2H_5OC_2H_5$.

Since it does not react with Na metal, it cannot be an alcohol.

$$C_2H_5OC_2H_5 + HI \rightarrow 2C_2H_5I + H_2O$$
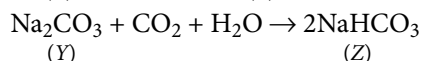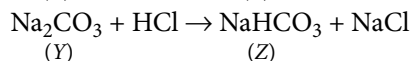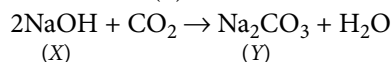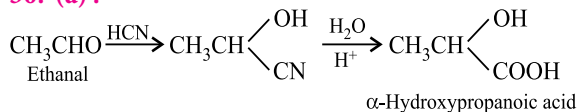$$\text{(excess)}$$

27. (a):

fac-   mer-
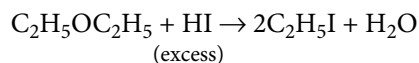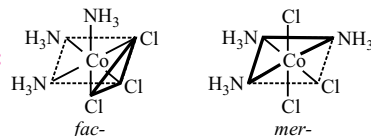
28. (a): Aldehydes are more reactive than ketones towards nucleophilic addition reactions. Aromatic aldehydes and ketones are less reactive than corresponding aliphatic aldehydes and ketones.
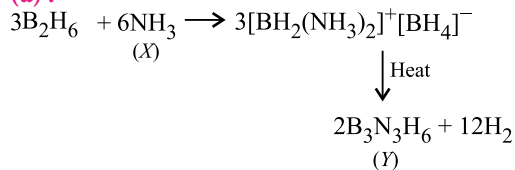
29. (a): $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$
$$\quad\quad (X)$$

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$
$$\quad (X) \quad\quad\quad\quad (Y)$$

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$
$$\quad (Y) \quad\quad\quad\quad (Z)$$

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$$
$$\quad (Y) \quad\quad\quad\quad\quad\quad\quad (Z)$$

30. (a):

α-Hydroxypropanoic acid

31. (a):

$$3B_2H_6 + 6NH_3 \longrightarrow 3[BH_2(NH_3)_2]^+[BH_4]^-$$
$$\quad\quad\quad\quad\quad\quad (X)$$

$$\downarrow \text{Heat}$$

$$2B_3N_3H_6 + 12H_2$$
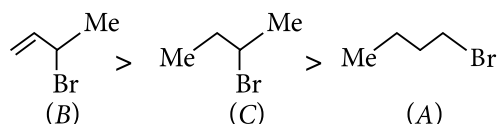$$\quad (Y)$$

32. (b): S_N1 reaction rate depends upon the stability of the carbocation, as carbocation formation is the rate determining step. Compound (B), forms a 2° allylic carbocation which is the most stable, the next stable carbocation is formed from (C), it is a 2° carbocation, (A) forms the least stable 1° carbocation, the order of reactivity is thus,

33. (a) : The decrease in the force of attraction exerted by the nucleus on the valence electrons due to presence of electrons in the inner shells is called shielding effect. A $4f$ orbital is nearer to the nucleus than $5f$ orbital. Hence shielding of $4f$ orbital is more than $5f$ orbital.

34. (b) : Ag and Au are extracted from their native ores by leaching (Mac - Arthur Forest cyanide process).
$$4M + 8CN^- + 2H_2O + O_2 \rightarrow 4[M(CN)_2]^- + 4OH^-$$
(where M = Ag or Au)
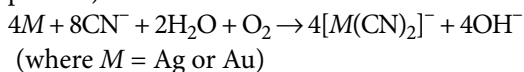
35. (d) : Electron affinity of Cl is maximum. The correct trend is Cl > F > Br > I.

36. (a) : $BaCl_2 \rightarrow Ba^{2+} + 2Cl^-$
$$\Lambda^\circ_{BaCl_2} = \Lambda^\circ_{Ba^{2+}} + 2\Lambda^\circ_{Cl^-} = 127 + (2 \times 76)$$
$$= 279 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$
Equivalent conductivity
$$= \frac{279}{2} = 139.5 \text{ ohm}^{-1}\text{cm}^2 \text{ eq}^{-1}$$

37. (b) : $d = \dfrac{Z \times M}{a^3 \times N_A}$
$$a^3 = \frac{Z \times M}{d \times N_A} = \frac{4 \times 58.5}{2.165 \times 6.023 \times 10^{23}}$$
$$a^3 = 179.5 \times 10^{-24} \text{ cm}^3$$
$$a = 5.64 \times 10^{-8} \text{ cm or } 564 \text{ pm}$$
Distance between Na^+ and Cl^-
$$= \frac{a}{2} = \frac{564}{2} = 282 \text{ pm}$$

38. (b) : Hydration enthalpy decreases with increase in ionic size down the group.
$$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$
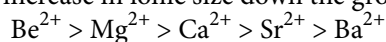
39. (a) : Except carbon halides, other halides are readily hydrolysed by water. In CX_4, the central atom cannot accommodate lone pair of electrons from oxygen atom of water molecule due to absence of d-orbitals.

40. (a) : This is Sandmeyer's reaction and the product Y is chlorobenzene.

41. (b) : $X = \dfrac{1}{2}(VE + MA - c + a)$

where, VE = No. of valence electrons on the central atom.
MA = No. of monovalent atoms surrounding the central atom.
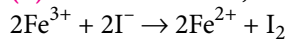
c = Charge on the cation
a = Charge on the anion

For NO_2^+, $X = \dfrac{1}{2}(5 + 0 - 1) = 2$ (sp hybrid orbitals)

For NO_3^-, $X = \dfrac{1}{2}(5 + 0 + 1) = 3$ (sp^2 hybrid orbitals)

For NH_4^+, $X = \dfrac{1}{2}(5 + 4 - 1) = 4$ (sp^3 hybrid orbitals)

42. (d) : For the reaction,
$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$$
$$E^\circ_{cell} = E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{I_2/I^-}$$
$$= 0.77 - (0.54) = + 0.23 \text{ V}$$
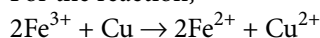Here, E°_{cell} is +ve so, reaction is feasible.
For the reaction,
$$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$$
$$E^\circ_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Cu^{2+}/Cu}$$
$$= 0.80 - (0.34) = + 0.46 \text{ V}$$
Here, E°_{cell} is +ve so, the reaction is feasible.
For the reaction,
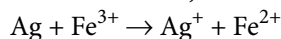$$2Fe^{3+} + Cu \rightarrow 2Fe^{2+} + Cu^{2+}$$
$$E^\circ_{cell} = E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{Cu^{2+}/Cu}$$
$$= 0.77 - (0.34) = + 0.43 \text{ V}$$
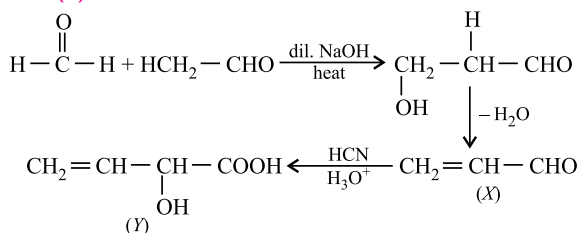Here, E°_{cell} is +ve so, the reaction is feasible.
For the reaction,
$$Ag + Fe^{3+} \rightarrow Ag^+ + Fe^{2+}$$
$$E^\circ_{cell} = E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{Ag^+/Ag}$$
$$= 0.77 - (0.80) = - 0.03 \text{ V}$$
Here, E°_{cell} is negative so, the reaction is not feasible.
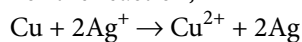
43. (a) :

44. (a) : Dinitrogen and dioxygen do not react with each other at a normal temperature. At high temperature (in an automobile engine) when fossil fuel is burnt, these gases combine to yield significant quantities of NO and NO_2.

45. (a) : 2-3% solution of iodine in alcohol-water mixture is known as tincture of iodine. It is a powerful antiseptic.

CBSE BOARD
PRACTICE PAPER 2015

Time allowed : 3 hrs.   **Maximum marks :** 70

GENERAL INSTRUCTIONS

- **(a)** All questions are compulsory.
- **(b)** Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- **(c)** Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- **(d)** Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
- **(e)** Q. no. 23 is a value based question and carries 4 marks.
- **(f)** Q. no. 24 to 26 are long answer questions and carry 5 marks each.
- **(g)** Use log tables if necessary use of calculators is not allowed.

1. Write the structure of 1-bromo-4-sec-butyl-2-methylbenzene.

2. For the reaction, $X_2 + 2Y_2 \rightarrow 2XY_2$, write the rate equation in terms of the rate of disappearance of Y_2.

3. Pick out the odd one amongst the following on the basis of their medicinal properties mentioning the reason.
   Chloroxylenol, phenol, chloramphenicol, bithional.

4. Aniline is a weaker base than cyclohexylamine. Why?

5. Account for the following : *o*-nitrophenol has lower boiling point than *p*-nitrophenol.

6. A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

7. Rate constant of the first order reaction is 6.93×10^{-3} s^{-1}. Calculate

   (i) half-life.

   (ii) time of 75% completion of reaction.

8. **(i)** Give the electronic configuration of the *d*-orbitals of Ti in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion in an octahedral crystal field.

   (ii) Why is the given complex coloured? Explain on the basis of distribution of electrons in the *d*-orbitals.

9. Predict the products of electrolysis obtained at the electrodes in each case when the electrodes used are of platinum:

   (i) An aqueous solution of AgNO_3.

   (ii) An aqueous solution of H_2SO_4.

10. Explain how vacancies are introduced in an ionic solid when a cation of higher valency is added as an impurity in it.

    OR

    Ionic solids, which have anionic vacancies due to metal-excess defect, develop colour. Explain with the help of a suitable example.

11. Give reasons for the following:
  (i) Addition of Cl_2 to KI solution gives it a brown colour, but excess of Cl_2 turns it colourless.
  (ii) Phosphinic acid behaves as a monoprotic acid.
  (iii) White phosphorus is much more reactive than red phosphorus.

12. (i) A given ore is a mixed sulphide of lead and zinc (PbS-ZnS). Suggest a method to separate the mixture.
  (ii) Write the chemical reactions involved in the extraction of gold by cyanide process.

13. Explain the following terms with a suitable example in each case:
  (i) Shape-selective catalysis
  (ii) Dialysis
  (iii) Multimolecular colloids

14. (i) Give the IUPAC name of $[PtCl(NH_2CH_3)(NH_3)_2]Cl$.
  (ii) Compare the magnetic behaviour of the complex entities $[Fe(CN)_6]^{4-}$ and $[FeF_6]^{3-}$. [Fe = 26].

15. A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential $(E^\circ_{Zn^{2+}/Zn} = -0.76 \text{ V})$

16. Write the structures of *A*, *B* and *C* in the following reactions.
  (i)

CH_3—CH—CH_3 (with Cl below) $\xrightarrow[\Delta]{\text{alc KOH}}$ A $\xrightarrow{\text{B}_2\text{H}_6}{\text{H}_2\text{O}_2/\text{OH}^-}$ ... C $\xleftarrow{\text{SOCl}_2}$ B ←

  (ii)

$\xrightarrow[\text{anhy AlCl}_3]{\text{CH}_3\text{COCl}}$ A $\xrightarrow{B}$ ... (ring with CH_2CH_3) $\xrightarrow[\text{OH}^-]{\text{KMnO}_4}$ C
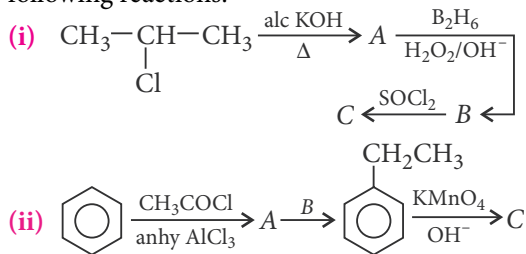
17. Write structures and names of the monomers of the following polymers :
  (i) Nylon 6,6   **(ii)** Nylon 6
  (iii) Urea formaldehyde resin

<center>**OR**</center>

  (i) How will you differentiate between low density and high density polythenes?

  (ii) Arrange the following polymers in order of increasing intermolecular forces: Bakelite, Nylon 6,6, Polythene, Neoprene.

18. State Henry's law for solubility of a gas in a liquid and give its important applications.

19. Give plausible explanation for each of the following:
  (i) There are two $—NH_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazone.
  (ii) Give the mechanism of esterification of carboxylic acids.

20. (i) What is the structural difference between a nucleoside and a nucleotide?
  (ii) "The two strands of DNA are not identical but are complementary." Explain.
  (iii) Differentiate between fibrous and globular proteins.

21. Mention the action of the following on the human body in bringing relief from a disease.
  (i) Brompheniramine
  (ii) Aspirin
  (iii) Equanil

22. Outline the principles of refining of metals by the following methods:
  (i) Zone refining
  (ii) van Arkel method
  (iii) Liquation method

23. Dr. Rachna – a dietician conducted a seminar for the students of class XII. She emphasized the importance of balanced diet for good health. She also discussed with students that under special conditions like for pregnant women, growing children and HIV/AIDS patients or heart patients, protein rich diet is recommended.
  (i) What values are displayed by Dr. Rachna?
  (ii) Why do HIV/AIDS or heart patients need a protein rich diet?
  (iii) Name some rich sources of proteins.
  (iv) What are the chief components of a balanced diet?

24. (i) Give one chemical test to distinguish between the following pairs of compounds:
   (a) Methylamine and dimethylamine
   (b) Ethanal and propanal
   (c) Benzoic acid and ethyl benzoate

   (ii) How will you bring about the following conversions in not more than two steps?
   (a) Benzene to *m*-nitroacetophenone
   (b) 2-Methylpropanol to 2-methylpropene

<div align="center">OR</div>

(i) An organic compound (*A*) [molecular formula $C_8H_{16}O_2$] was hydrolysed with dilute sulphuric acid to give a carboxylic acid (*B*) and an alcohol (*C*). Oxidation of (*C*) with chromic acid produced (*B*). (*C*) on dehydration gives but-1-ene. Write equations for the reactions involved.

(ii) Write the equations involved in the following reactions:
   (a) Kolbe's reaction
   (b) Cannizzaro reaction

25. (i) Why is freezing point depression of 0.1 M sodium chloride solution nearly twice that of 0.1 M glucose solution?

(ii) At 300 K, 36 g of glucose present per litre in its solution has an osmotic pressure of 4.98 bar. If osmotic pressure of solution is 1.52 bar at the same temperature, what would be its concentration?

(iii) Osmotic pressure is more useful to calculate molecular mass than other colligative properties. Why?

<div align="center">OR</div>

(i) 15 g of an unknown molecular mass substance was dissolved in 450 g of water. The resulting solution freezes at – 0.34°C. What is the molar mass of the substance? (K_f for water = 1.86 K kg mol^{-1})

(ii) Non-ideal solutions exhibit either positive or negative deviations from Raoult's law. What are these deviations and why are they caused? Explain with one example for each type.
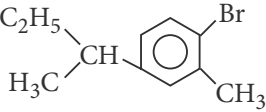
26. Assign reason for the following:
   (i) The enthalpies of atomisation of transition elements are high.
   (ii) The transition metals and many of their compounds act as good catalyst.
   (iii) Actinoid contraction is greater from element to element than the lanthanoid contraction.
   (iv) The E^o value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}.
   (v) Scandium ($Z = 21$) does not exhibit variable oxidation states and yet it is regarded as transition element.

<div align="center">OR</div>

(i) Write the steps involved in the preparation of
   (a) $K_2Cr_2O_7$ from Na_2CrO_4
   (b) $KMnO_4$ from K_2MnO_4.

(ii) What is meant by lanthanoid contraction? What effect does it have on the chemistry of the elements which follow lanthanoid contraction?

<div align="center">

SOLUTIONS

</div>

1.

2. Rate of reaction = $-\dfrac{1}{2}\dfrac{d[Y_2]}{dt}$

3. Chloramphenicol is an antibiotic while all the remaining are antiseptics.

4. In aniline there is delocalisation of lone pair of electrons of N atom in benzene ring therefore it is less basic than cyclohexylamine.

5. *o*-Nitrophenol has intramolecular H-bonding which is weaker than intermolecular H-bonding present in *p*-nitrophenol.

6. No. of atoms in the close packing = 0.5 mol
= $0.5 \times 6.022 \times 10^{23} = 3.011 \times 10^{23}$
No. of octahedral voids = $1 \times$ No. of atoms in the packing = 3.011×10^{23}
No. of tetrahedral voids = $2 \times$ No. of atoms in the packing = $2 \times 3.011 \times 10^{23} = 6.022 \times 10^{23}$

Total no. of voids $= 3.011 \times 10^{23} + 6.022 \times 10^{23}$
$$= 9.033 \times 10^{23}$$

7. **(i)** For first order reaction,
    $$\text{half-life} = \frac{0.693}{k} = \frac{0.693}{6.93 \times 10^{-3}\,\text{s}^{-1}} = 100 \text{ s}$$

    (ii) For first order reaction, half-life is related to time of 75% completion of reaction by
    $$t_{75} = 2 \times \text{half-life} = 2 \times 100 = 200 \text{ s}$$

8. **(i)** In $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion, Ti is in +3 oxidation state. The electronic configuration of Ti^{3+} ion is $3d^1$. In an octahedral field, it is $t_{2g}^1 e_g^0$.

    (ii) Due to $d\text{-}d$ transition, the electron present in t_{2g} absorbs green and yellow radiation of white light for excitation to e_g. The complementary colour is purple.

9. **(i)** $\text{AgNO}_{3(aq)} \longrightarrow \text{Ag}^+_{(aq)} + \text{NO}^-_{3(aq)}$
    $\text{H}_2\text{O}_{(l)} \longrightarrow \text{H}^+_{(aq)} + \text{OH}^-_{(aq)}$
    At cathode: $\text{Ag}^+_{(aq)} + e^- \longrightarrow \text{Ag}_{(s)}$
    At anode: $2\text{OH}^-_{(aq)} \longrightarrow \text{O}_2 + 2\text{H}^+_{(aq)} + 4e^-$
    Or $2\text{H}_2\text{O}_{(l)} \longrightarrow \text{O}_2 + 4\text{H}^+_{(aq)} + 4e^-$

    (ii) $\text{H}_2\text{SO}_{4(aq)} \longrightarrow 2\text{H}^+_{(aq)} + \text{SO}^{2-}_{4(aq)}$
    $\text{H}_2\text{O}_{(l)} \longrightarrow \text{H}^+_{(aq)} + \text{OH}^-_{(aq)}$
    At cathode: $2\text{H}^+_{(aq)} + 2e^- \longrightarrow \text{H}_{2(g)}$
    At anode: $2\text{OH}^-_{(aq)} \longrightarrow \text{O}_2 + 2\text{H}^+_{(aq)} + 4e^-$
    Or $2\text{H}_2\text{O}_{(l)} \longrightarrow \text{O}_2 + 4\text{H}^+_{(aq)} + 4e^-$

10. When a cation of higher valency is added as an impurity in the ionic solid, some of the sites of the original cations are occupied by the cations of higher valency. Each cation of higher valency replaces two or more original cations and occupies the site of one original cation and the other site(s) remains vacant.
    Cationic vacancies produced =
    Number of cations of higher valency × Difference in valencies of the original cation and cation of higher valency

    ### OR

    In ionic solids with anionic vacancies due to metal-excess defect, when the metal atoms deposit on the surface, they diffuse into the crystal and after ionization, the metal ion occupies cationic vacancy while electron occupies anionic vacancy. These electrons get excited to higher energy levels by absorption of suitable wavelengths from the visible white light and, therefore appear coloured.
    Example: Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.
    $$\text{ZnO} \xrightarrow{\text{Heat}} \text{Zn}^{2+} + \frac{1}{2}\text{O}_2 + 2e^-$$
    The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites. These electrons absorb visible light and impart yellow colour to zinc oxide.
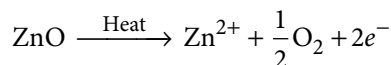
11. **(i)** Chlorine being stronger oxidising agent than iodine displaces iodine from KI which brings brown colour to the solution. In excess of chlorine, the liberated iodine is further oxidised to iodic acid and solution becomes colourless.
    $\text{Cl}_2 + 2\text{KI} \longrightarrow 2\text{KCl} + \text{I}_2$;
    (Brown)
    $\text{I}_2 + 5\text{Cl}_2 + 6\text{H}_2\text{O} \longrightarrow 2\text{HIO}_3 + 10\text{HCl}$
    (Colourless)
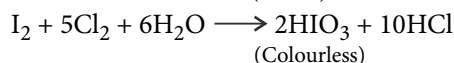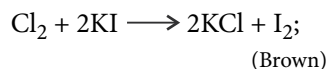
    (ii) Phosphinic acid has only one replaceable hydrogen atom.

    $$\underset{\displaystyle \text{H}}{\overset{\displaystyle \overset{\textstyle \text{O}}{\underset{\textstyle |\!|}{}}}{\text{HO}-\text{P}-\text{H}}}$$
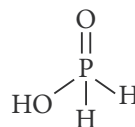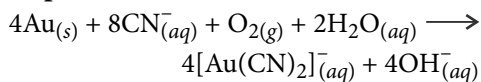
    (iii) White P_4 is monomeric whereas red phosphorus is polymeric. White P_4 has less bond dissociation energy than red P_4.

12. **(i)** PbS and ZnS both form froth with pine oil on bubbling air inside the mixture. In such case NaCN is used as a depressant.
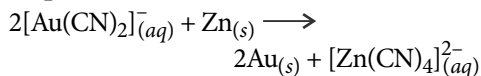   Before froth floatation process is used, NaCN is mixed (as a depressant) which forms a complex with ZnS.
    $\text{ZnS} + 4\text{NaCN} \longrightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + \text{Na}_2\text{S}$
    PbS remains insoluble and is separated. CuSO_4 is then added to activate depressed ZnS and air is blown when ZnS floats. This method is called differential floatation.

(ii) Step I:

$$4Au_{(s)} + 8CN^-_{(aq)} + O_{2(g)} + 2H_2O_{(aq)} \longrightarrow$$
$$4[Au(CN)_2]^-_{(aq)} + 4OH^-_{(aq)}$$

Step II:

$$2[Au(CN)_2]^-_{(aq)} + Zn_{(s)} \longrightarrow$$
$$2Au_{(s)} + [Zn(CN)_4]^{2-}_{(aq)}$$

13. (i) Shape-selective catalysis: The catalytic reaction which depends upon the pore size of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis. Zeolites are good shape-selective catalysts because of their honey comb-like structures.

(ii) Dialysis: The process of separating a crystalloid from a colloid by filteration or diffusion through a membrane is called dialysis. The apparatus employed to affect such a separation is known as dialyser.

Purification of blood in the artificial kidney machine.

(ii) Multimolecular colloids: A large number of atoms or smaller molecules of a substance on dissolution aggregate together to form species having size (diameter < 1 nm) in the colloidal range (1–1000 nm). Such species are known as multimolecular colloids. For example, a sulphur sol consists of particles containing a thousand or more of S_8 sulphur molecules.

14. (i) Diamminechlorido(methylamine) platinum(II) chloride

(ii) (a) $[Fe(CN)_6]^{4-}$ ion
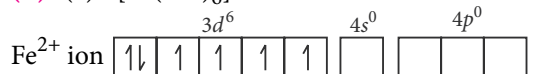
Fe^{2+} ion

Fe^{2+} ion hybridised (under the influence of strong field ligand).

Six empty d^2sp^3 hybrid orbitals

$[Fe(CN)_6]^{4-}$ ion formation :

Six pairs of electrons from six CN^- ions.

Since the complex ion does not contain any unpaired electron, so it is diamagnetic.

(b) $[FeF_6]^{3-}$ ion

Fe^{3+} ion

Fe^{3+} ion hybridised (under the influence of weak field ligand).
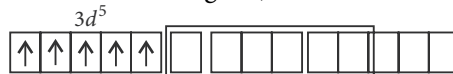
Six empty sp^3d^2 hybrid orbitals

$[FeF_6]^{3-}$ ion formation :

Six electron pairs from six F^- ions

As the complex ion contains five unpaired electrons, it is highly paramagnetic in nature.

$$\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.9 \text{ BM}$$

15. The electrode reaction written as reduction reaction is

$$Zn^{2+} + 2e^- \rightarrow Zn(n = 2)$$
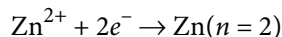
Applying Nernst equation, we get

$$E_{Zn^{2+}/Zn} = E°_{Zn^{2+}/Zn} - \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}]}$$

As 0.1 M $ZnSO_4$ solution is 95% dissociated, this means that in the solution,

$$[Zn^{2+}] = \frac{95}{100} \times 0.1 \text{ M} = 0.095 \text{ M}$$

$$\therefore E_{Zn^{2+}/Zn} = -0.76 - \frac{0.0591}{2} \log \frac{1}{0.095}$$

$$= -0.76 - 0.02955 (\log 1000 - \log 95)$$
$$= -0.76 - 0.02955 (3 - 1.9777)$$
$$= -0.76 - 0.03021$$
$$= -0.79021 \text{ V}$$

16. (i)

$$CH_3-CH-CH_3 \xrightarrow[\Delta]{\text{alc KOH}} CH_3-CH=CH_2$$
$$\quad\quad\quad |$$
$$\quad\quad\quad Cl \quad\quad\quad\quad\quad\quad\quad (A)$$

$$H_2O_2/OH^- \Big\downarrow B_2H_6$$

$$CH_3CH_2CH_2Cl \xleftarrow{SOCl_2} CH_3CH_2CH_2OH$$
$$(C) \quad\quad\quad\quad\quad\quad (B)$$

(ii)
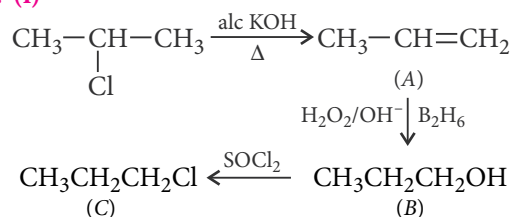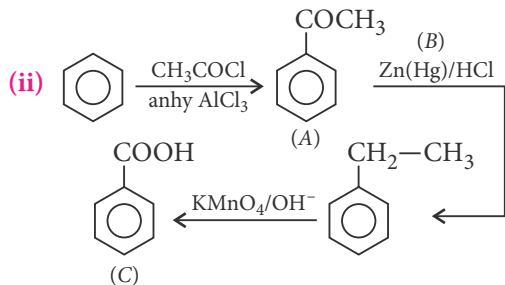
17. (i) $HOOC(CH_2)_4COOH$ and $NH_2(CH_2)_6NH_2$
　　　　Adipic acid　　　　　　Hexamethylene
　　　　　　　　　　　　　　　　diamine

(ii)

Caprolactam
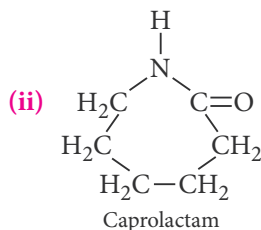
(iii) NH_2CONH_2 and $HCHO$
　　　　Urea　　　　Formaldehyde

OR

(i)

Low density polythene	High density polythene
1. It is tough but flexible.	It is tougher and harder.
2. Highly branched structure so, it has low density.	It is linearly arranged and has a high density due to close packing.

(ii) Neoprene < Polythene < Nylon 6,6 < Bakelite

18. Henry's law: Mole fraction of a gas in the solution is proportional to the partial pressure of the gas over the solution.
Applications of Henry's law:
(i) Soft drinks and soda water bottles are sealed under high pressure to increase the solubility of CO_2.
(ii) The tanks used by scuba divers [persons swimming under water use underwater breathing apparatus known as scuba] are filled with air diluted with helium.

19. (i)

Semicarbazide
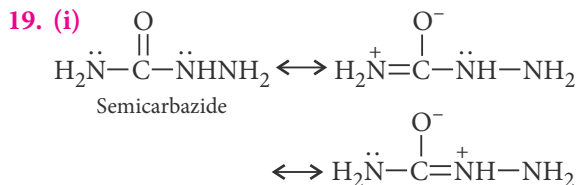
As electron density on one $-NH_2$ group decreases due to resonance it does not act as a nucleophile while the lone pair of electrons on the other NH_2 group (*i.e.*, attached to NH) is not involved in resonance and hence is available for nucleophilic attack on the C=O group of aldehydes and ketones.

(ii) Mechanism of esterification: It is a nucleophilic acyl substitution.
(a) Protonation of carboxyl oxygen:
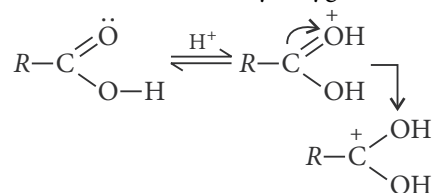
(b) Nucleophilic addition of alcohol:

Tetrahedral intermediate
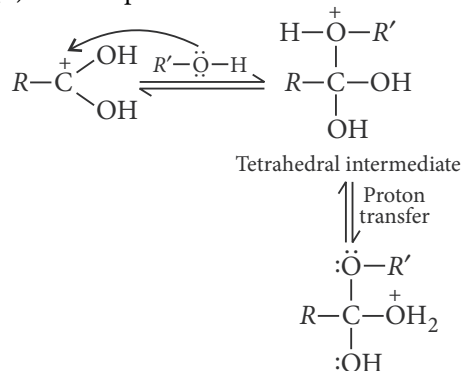
(c) Elimination of water molecule:
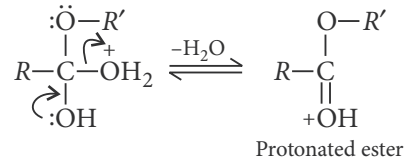
Protonated ester

(d) Protonated ester loses a proton to give ester:

Ester

20. (i) A unit formed by attachment of a base to C-1′ position of sugar is known as nucleoside.

When nucleoside is linked to phosphoric acid at C-5′ position of sugar moiety, resulting species is called nucleotide.

Nucleoside   Nucleotide
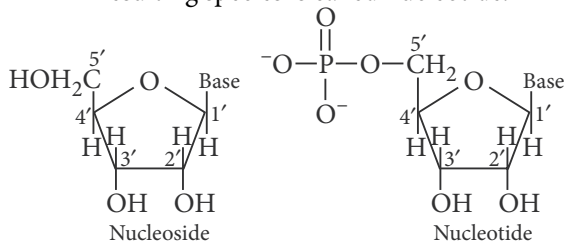
(ii) James Watson and Francis Crick gave a double strand helix structure for DNA. Two nucleic acid chains are bonded to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine (A=T) whereas cytosine forms hydrogen bonds with guanine (C≡G).

(iii)

Fibrous protein	Globular protein
Elongated, insoluble in water because of hydrophobic *R* group *e.g.* keratin, collagen	Spherical, water soluble because of hydrophilic amino acids with polar *R* group *e.g.* enzymes, antibodies and haemoglobin

21.

S. No.	Drug	Effect
(i)	Brompheniramine	Antiallergic, it inferes with the natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect.
(ii)	Aspirin	Pain reliever and antipyretic
(iii)	Equanil	For controlling depression and hypertension

22. (i) Zone refining: The method is based on the difference in solubility of impurities in molten and solid state of the metal.

(ii) van Arkel method : In this method, impure metal is converted to a volatile compound while the impurities are not affected. The volatile compound is then decomposed to get pure metal.

(iii) Liquation method : This process is based on the difference in fusibility of metal and impurities. Impure metal is gently heated on the sloping hearth of a furnace. The metal melts and flows down leaving behind the impurities on the hearth.

23. (i) Dr. Rachna, showed concern towards the health needs of students.

(ii) Protein rich diet helps to strengthen the immune system of HIV/AIDS patients and helps to reduce blood pressure as well as cholesterol of heart patients.

(iii) Eggs, sprouts, beans, lentils are rich sources of proteins.

(iv) Carbohydrates, fats and proteins are basic components of a balanced diet.
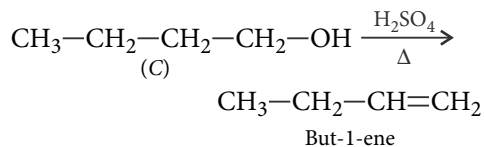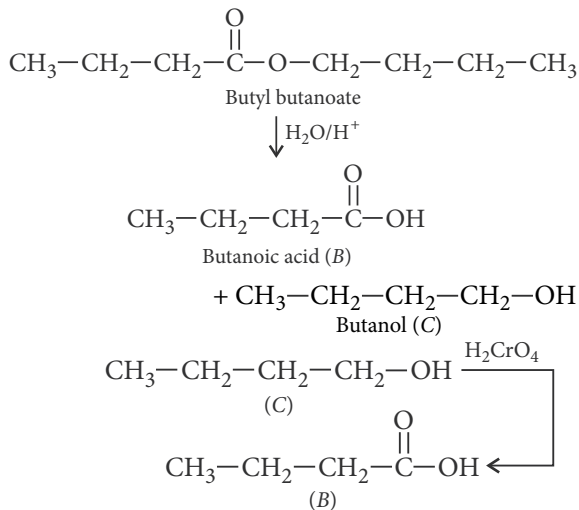
24. (i) (a) Methylamine and dimethylamine can be distinguished by carbylamine test. Methylamine, a primary amine, gives offensive smell on heating with chloroform and alcoholic solution of KOH whereas dimethylamine does not react.

(b) Ethanal and propanal can be distinguished by iodoform test. Yellow precipitate of iodoform will be formed from ethanal on heating with iodine and sodium hydroxide solution whereas propanal does not give iodoform test.

(c) Benzoic acid and ethyl benzoate can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with $NaHCO_3$ whereas ethyl benzoate does not react.
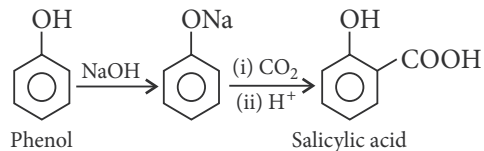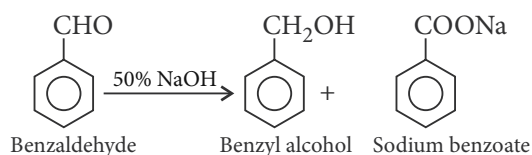
(ii) (a)

Benzene → Acetophenone (CH$_3$—C—Cl, anhy AlCl$_3$)

Acetophenone → *m*-Nitroacetophenone (Conc. HNO$_3$, Conc. H$_2$SO$_4$)

(b)

$$CH_3-CH-CH_2OH \xrightarrow{SOCl_2}$$

2-Methylpropanol (with CH$_3$ branch)

$$CH_3-C=CH_2 \xleftarrow{alc.\ KOH} CH_3-CH-CH_2-Cl$$

2-Methylpropene ← (CH$_3$ branch)
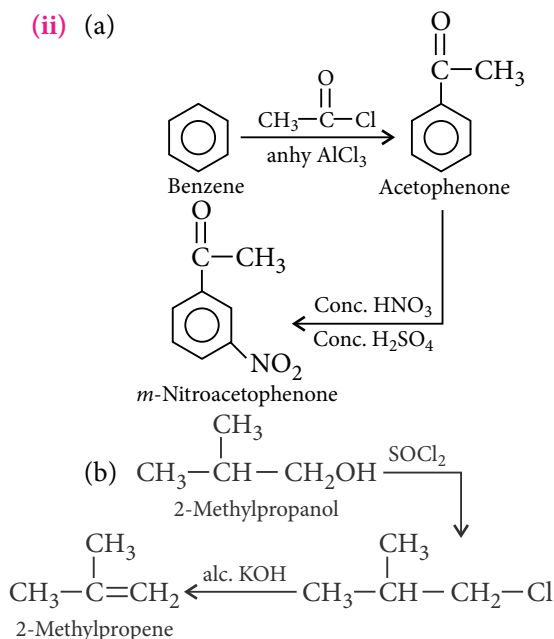
OR

(i) Compound '*A*' (C$_8$H$_{16}$O$_2$) on hydrolysis gives an acid '*B*' and an alcohol '*C*'. It shows that '*A*' is an ester. Since the oxidation of alcohol '*C*' also gives the acid '*B*' indicates that '*B*' and '*C*' both contain same number of carbon atoms, *i.e.*, four carbon atoms each and same arrangement of atoms. Formation of but-1-ene on dehydration of '*C*' indicates it to be butan-1-ol, so the possible ester (*A*) could be butyl butanoate.

$$CH_3-CH_2-CH_2-\overset{O}{\overset{||}{C}}-O-CH_2-CH_2-CH_2-CH_3$$
Butyl butanoate

$$\downarrow H_2O/H^+$$

$$CH_3-CH_2-CH_2-\overset{O}{\overset{||}{C}}-OH$$
Butanoic acid (*B*)

$$+ CH_3-CH_2-CH_2-CH_2-OH$$
Butanol (*C*)

$$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow{H_2CrO_4}$$
(*C*)

$$CH_3-CH_2-CH_2-\overset{O}{\overset{||}{C}}-OH$$
(*B*)

$$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow[\Delta]{H_2SO_4}$$
(*C*)

$$CH_3-CH_2-CH=CH_2$$
But-1-ene

(ii) (a) Kolbe's reaction:

Phenol → (NaOH) → ONa → (i) CO$_2$ (ii) H$^+$ → Salicylic acid (OH, COOH)

(b) Cannizzaro reaction:

Benzaldehyde (CHO) → (50% NaOH) → Benzyl alcohol (CH$_2$OH) + Sodium benzoate (COONa)

25. (i) Sodium chloride being a strong electrolyte completely dissociates in the solution while glucose does not dissociate. The number of particles in sodium chloride solution becomes double than that of glucose solution. Hence freezing point depression of sodium chloride is nearly twice that of glucose solution of same molarity, because it is a colligative property.

(ii) $\pi = CRT$

R and T are same in both cases hence

$$\frac{\pi_1}{\pi_2} = \frac{C_1}{C_2} \text{ or, } C_2 = \frac{\pi_2 C_1}{\pi_1}$$

Molarity of first solution

$$C_1 = \frac{36}{180} = 0.2 \text{ mol L}^{-1}$$

$$C_2 = \frac{\pi_2 C_1}{\pi_1} = \frac{1.52 \times 0.2}{4.98} = 0.0610 \text{ M}$$

(iii) Magnitude of osmotic pressure is large even for very dilute solutions and it can be measured at room temperature hence it is more useful for the calculation of molecular mass.

OR

(i) Given: $w_2 = 15$ g, $w_1 = 450$ g

$K_f = 1.86$ K kg mol^{-1}, $M_2 = $?

$\Delta T_f = 0 - (-0.34) = 0.34$°C or 0.34 K

Now, $\Delta T_f = K_f \cdot m$

$$\Rightarrow \quad \Delta T_f = K_f \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

$$\Rightarrow \quad M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1}$$

$$\Rightarrow \quad M_2 = \frac{1.86 \times 15 \times 1000}{0.34 \times 450}$$

$$M_2 = 182.35 \text{ g mol}^{-1}$$

(ii) When the vapour pressure of a non-ideal solution is either higher or lower than that predicted by Raoult's law, the solution exhibits deviation.

These deviations are caused because of unequal intermolecular attractive forces between solute-solvent molecules and solute-solute or solvent-solvent molecules.

Examples of positive deviations : Mixture of ethanol and acetone, carbon disulphide and acetone.

Examples of negative deviations : Chloroform and acetone, nitric acid and water.

26. (i) As transition metals have a large number of unpaired electrons in the d-orbitals of their atoms they have strong interatomic attractions or metallic bonds. Hence they have high enthalpy of atomization.

(ii) Many transition metals and their compounds act as catalysts. The catalytic activity is due to their ability to exhibit multiple oxidation states. For example, V_2O_5 in Contact process and finely divided iron in Haber process.

(iii) The actinoid contraction is more than lanthanoid contraction due to poor shielding by $5f$-electrons than by $4f$-electrons.

(iv) Much larger third ionisation energy of Mn(where change is d^5 to d^4) is mainly responsible for this. This also explains that +3 state of Mn is of little importance.

(v) Scandium $(Z = 21)$ has incompletely filled $3d$-orbitals in the ground state $(3d^1)$. Hence it is considered as a transition element.

OR

(i) (a) $2Na_2CrO_4 + H_2SO_4 \longrightarrow$
Sod. chromate
$$Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$
Sod. dichromate
$$Na_2Cr_2O_7 + 2KCl \longrightarrow$$
$$K_2Cr_2O_7 + 2NaCl$$
Pot. dichromate

(b) The potassium manganate is oxidised to potassium permanganate by oxidation with chlorine.
$$2K_2MnO_{4(aq)} + Cl_{2(g)} \rightarrow 2KMnO_{4(aq)} + 2KCl_{(g)}$$

(ii) Lanthanoid contraction: The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction.

It is caused due to imperfect shielding of nuclear charge by $4f$-electrons.

Lanthanum (La) has the largest ionic radius while lutetium (Lu) has the smallest among the $4f$-series elements.

Consequences of lanthanoid contraction:

(a) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.

(b) Atomic and ionic sizes of $4d$ transition series elements and $5d$ series elements are similar. *e.g.* Atomic radii of zirconium(Zr) is same as that of hafnium(Hf).

··· ■■

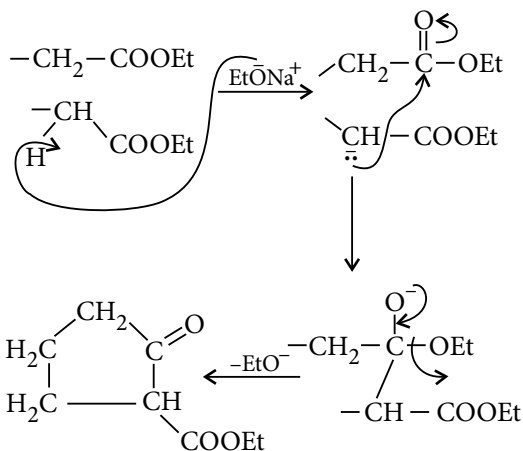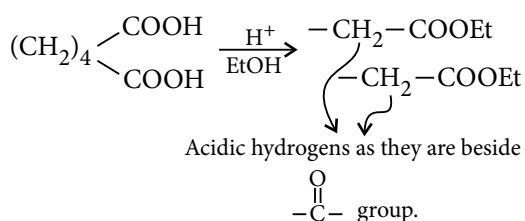| IMPORTANT EXAMINATION DATES 2015			
4 April	JEE (Main-Offline)	29-30 April	Karnataka CET
10 – 11 April	JEE (Main-Online)	3 May	AIPMT
8 – 19 April	VITEEE	10 May	COMED K
18-19 April	WB JEE	16 May	UPSEAT
19 April	MGIMS	24 May	JEE Advanced
20-21April	Kerala PET	1 June	AIIMS
22-23 April	Kerala PMT	7 June	JIPMER

CONCEPT BOOSTER

Dear students, as promised solutions of JEE Advanced Practice Paper in organic chemistry, Feb'15, Page No. 25 are given in this issue. All the best for the board examinations. Take care all of you. Good bye !!
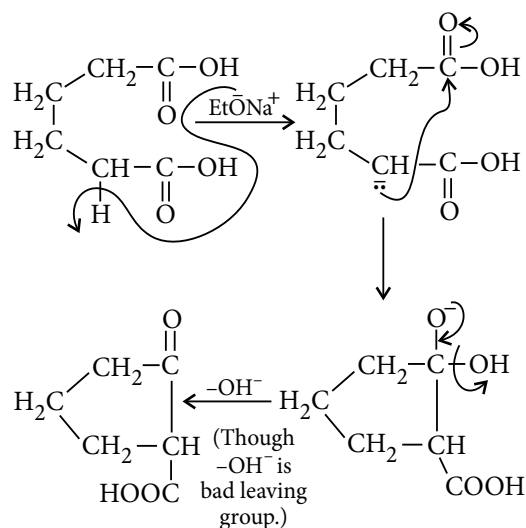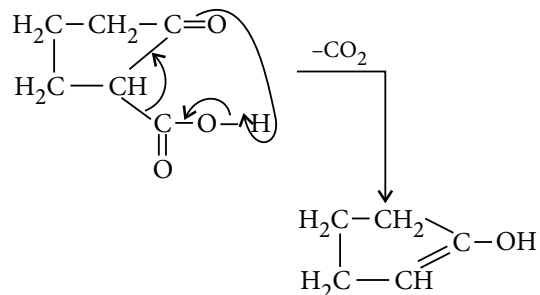
*Arunava Sarkar

1. **(d):** $(CH_2)_4 \big\langle {}^{COOH}_{COOH} \xrightarrow{H^+, EtOH} \xrightarrow{Et\bar{O}Na^+}$?
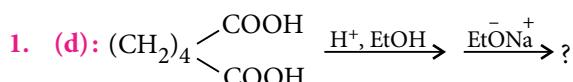
This is straight away Dieckmann synthesis.

$(CH_2)_4 \big\langle {}^{COOH}_{COOH} \xrightarrow[EtOH]{H^+}$ $-CH_2-COOEt$ / $-CH_2-COOEt$

Acidic hydrogens as they are beside

$-\overset{O}{\overset{\|}{C}}-$ group.

After this, EtO$^-$Na$^+$ is ready for more attack but no other reagents are provided for further attack. Hence the reaction stops here. In the question, $-COOH$ will remain in the form of $-COOH$.

This is a β-keto carboxylic acid.

This does not match with any of the options given in (a), (b) or (c). Therefore answer is (d).

* Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna 09732313208

2. (d):

2CH₂(COOEt)₂ with acidic hydrogens →(2NaOEt/EtOH)→ 2[NaĊH(COOEt)₂] (A)

→ (CH₂I₂, S_N2)

CH₂[CH(COOEt)₂][CH(COOEt)₂] (B)

→ strong base alcohol (Acidic hydrogens will be abstracted.) →

2Na⁺[H₂C with C̈(COOEt)₂ groups] (C)

→ CH₂Br–CH₂Br, S_N2 (x)

EtOOC–C(CH₂)(CH₂)–C(COOEt) ring (EtOOC groups) →(dil. KOH)→ KOOC/COOK ring (D)

→ H₃O⁺

HOOC–C(CH₂)(CH₂)–C–COOH ring →(Δ, –2CO₂)→ HOOC...HOOC cyclopentane (E)

3. (b): For this follow retro pinacol-pinacolone principle and then pinacol-pinacolone rearrangement.
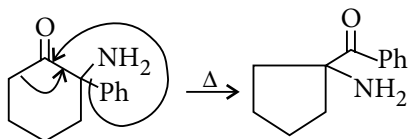
4. (c): LDA is a bulky base (strong also). So, kinetically controlled product will be largely predominant.

Kinetic enolate → (Me₃Si–Cl) → 99%
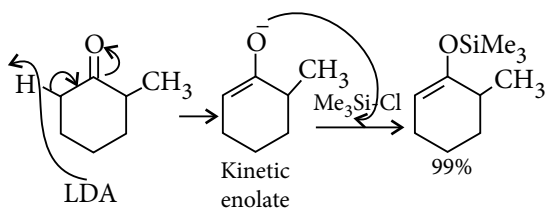
Thermodynamically controlled product will be just 1%.

i.e. is 1%.

5. (c):

CH₃–C=O with H–CH₂ →(enolisation)→ CH₃–C–O–H with H₂C

→ O=Se with O–H, O–H

CH₃–C=O with CH–O–Se–OH, H

→ (–H₂O)

H₂O + Se + CH₃–C=O with H–C=O
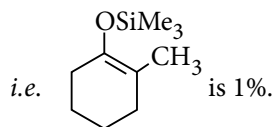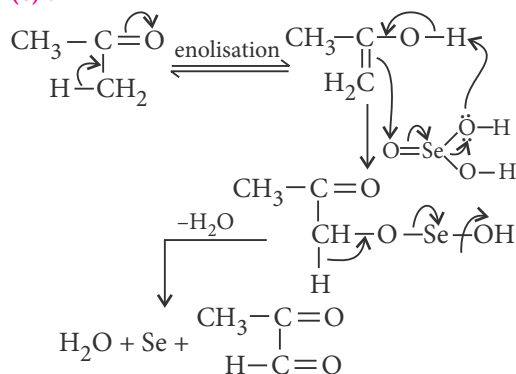
6. (a): If it would have been CH₃CHO then abstraction of H⁺ would have been easy. It is really tough to break a >C–D bond but with OH⁻ it is manageable.

ŌH + D–CD₂–CHO ⇌

[:C̈D₂–C=O with H ↔ CD₂=C–Ō with H]

H–C(=O)–H + :CD₂CHO → H–C(Ō)(H)–CD₂CHO

→ H₂O

HOH₂C–C(CH₂OH)(CH₂OH)–CHO ←(Similarly)— H–C(OH)(H)–CD₂CHO
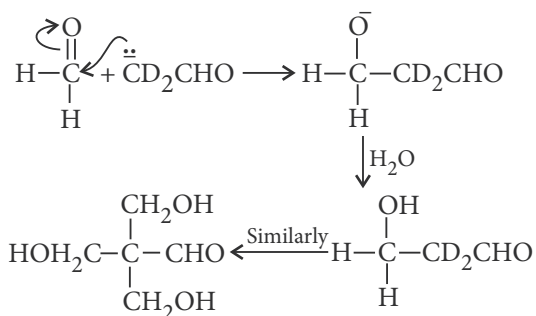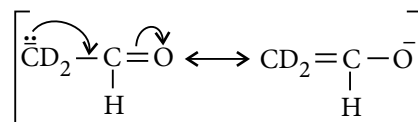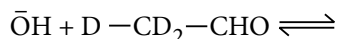
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After the formation of $HOH_2C-\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_2OH}{|}}{C}}-CHO$ reaction will proceed as below:

$HOH_2C-\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_2OH}{|}}{C}}-CH_2OH$

7. (d):
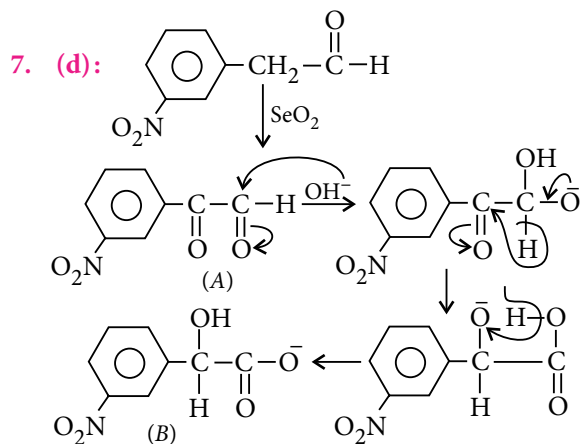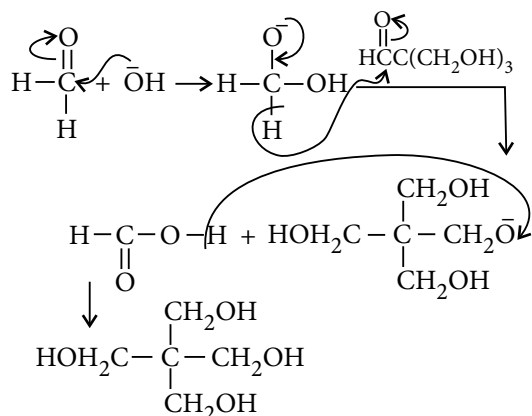
8. (b): Oxidised and reduced products of both the reactants will be involved.

9. (a):

$CH_3CH_2-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_2CH-\overset{+}{S}Me_2$
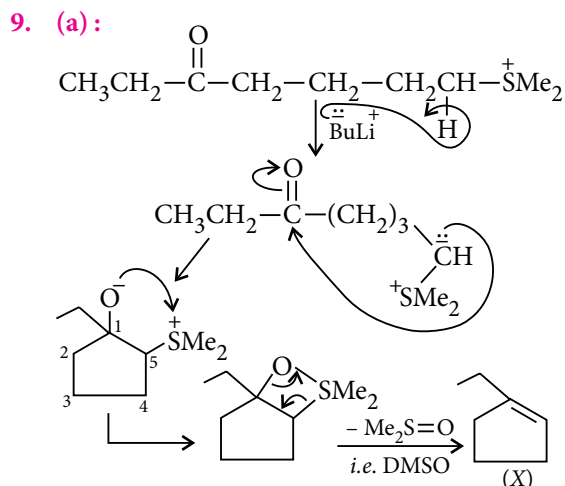
10. (b): Here syn-elimination will take place.
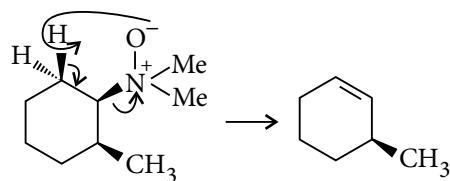
11. (d):

$(6\,\alpha\text{-H})$

$(5\,\alpha\text{-H})$
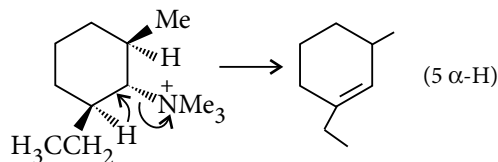
First one is the major product.

This type of elimination takes place *via* TS (concerted path). There is no chance of rearrangement of carbocation.

12. (c): MnO_2 oxidises allylic and benzylic alcohols.

13. (d):
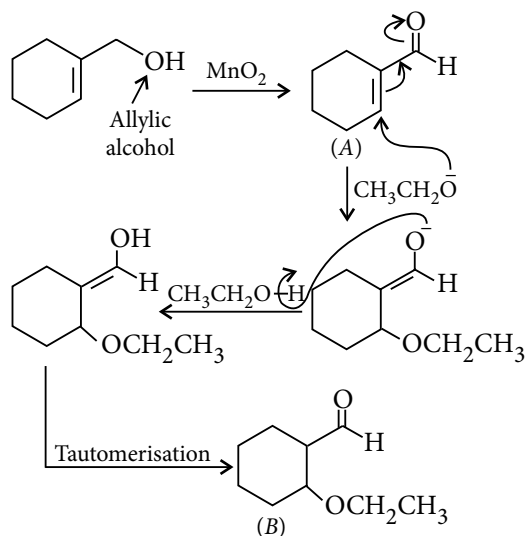
14. (b): This is Birch reduction and $-NO_2$ is *EWG*. Therefore, *ortho* and *para* positions become electron deficient.

So, $2Na \longrightarrow 2Na^+ + 2e^-$

–ve charge is stabilised here.
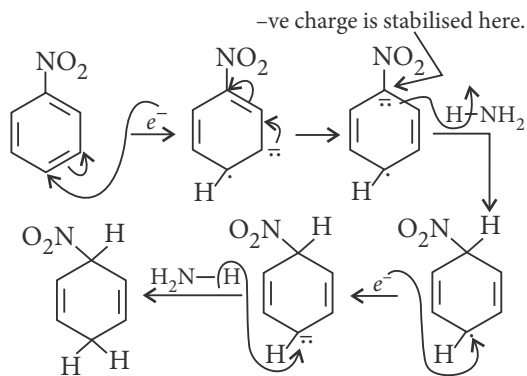
15. (c) : An *EDG* will make *meta* position electron deficient.

$$2Na \longrightarrow 2Na^+ + 2e^-$$

16. (c) :

17. (a) :
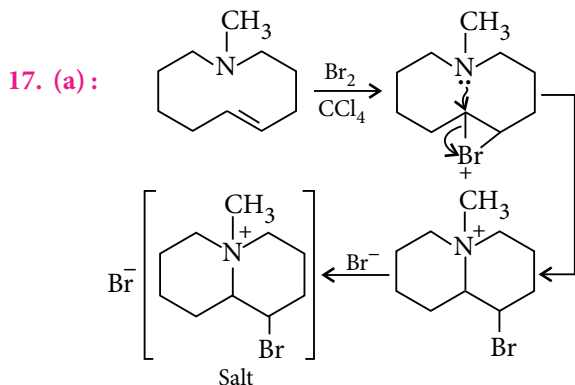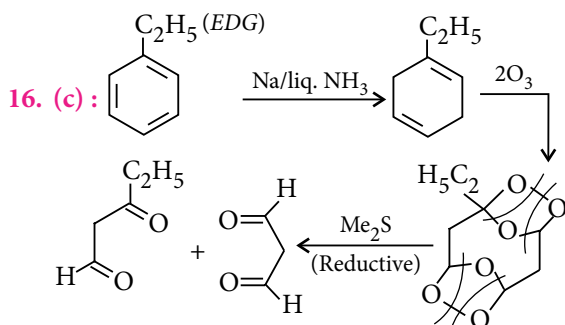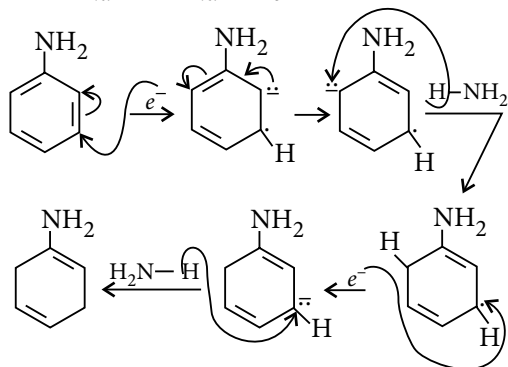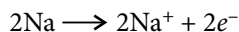
Release of $\overset{+}{C}H_3$ is not possible as it is not stable carbocation. Br^- also cannot attack as the reaction centre is crowded.
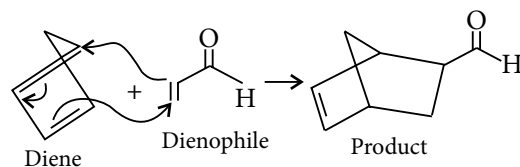
18. (b) : H_2, Pd/alcohol will definitely reduce double bond. It will reduce $-NO_2$ too.

19. (d) : H_2, Pd/C does not affect carbonyl group normally.

20. (a) :
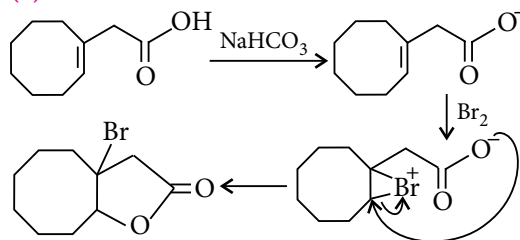
21. (d) : It is Diels-Alder reaction.

Diene   Dienophile   Product

....

22. (a) :

$$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2 - H \quad \overset{\cdot\cdot}{N}H_2$$

Acidic

$$\left[CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - \overset{\cdot\cdot}{C}H_2 \longleftrightarrow CH_3 - \overset{\overset{\displaystyle O^-}{|}}{C} = CH_2 \right]$$

(A)
More stable

$H - C \equiv C - H$

Tautomerises

$$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3 \quad\longleftarrow\quad CH_3 - \overset{\overset{\displaystyle O - H}{|}}{C} = CH_2$$

$+ H - C \equiv \overset{\cdot\cdot}{C}$

$$CH_3 - \overset{\overset{\displaystyle C \equiv CH}{|}}{\underset{\underset{\displaystyle O^-}{|}}{C}} - CH_3 \quad\xrightarrow{H^+ Cl^-}\quad CH_3 - \overset{\overset{\displaystyle C \equiv CH}{|}}{\underset{\underset{\displaystyle O - H}{|}}{C}} - CH_3$$

(B) (C)

$Pd \mid H_2$ (1 mole)

$$CH_3 - \overset{\overset{\displaystyle CH = CH_2}{|}}{\underset{\underset{\displaystyle O - H}{|}}{C}} - CH_3$$

(D)

$\xrightarrow[\text{Dehydration}]{Al_2O_3, 400°C}$

$$H_2C = \overset{\overset{\displaystyle CH_3}{|}}{C} - CH = CH_2$$
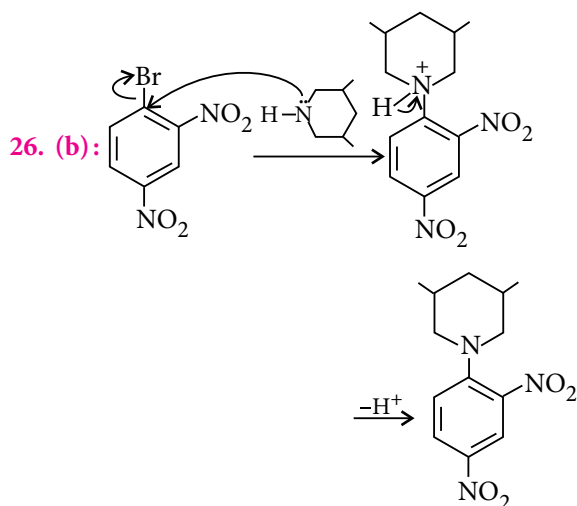
(E)

23. (c) : Those which will give positive iodoform test are acetophenone, ethanol, 2-butanol, ethanal, phenylacyl iodide $\left(Ph - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2I \right)$.

24. (a) : It is selective epoxidation. Epoxidation takes place at the olefin bond which is more electron rich.

25. (a)

26. (b) :

(chemical mechanism showing bromodinitrobenzene reacting with piperidine to form N-substituted dinitrobenzene, then $-H^+$)

27. (b) : $-SO_3H$ is *para* to the leaving group $-F$.

**28. (a) :** Reaction proceeds via elimination-addition (Benzyne mechanism).

29. (a) : $-OH$ is activating, $-CHO$ deactivating. So, reaction proceeds as per $-OH$ group *i.e.* *ortho* and *para* positions. *Para* being major (one side *ortho* is blocked).

30. (c) : $-CHO$ shows some extent of $-I$ effect which destabilises *ortho* position (with respect to $-OH$ *para* position) more.

31. (d) : When $\overset{+}{N}O_2$ will attack the middle ring then the complex formed will be stabilised more than the other two cases.

32. (a) : $-Cl$ is *ortho-para* directing but deactivating.

33. (d) :

(mechanism showing electrophilic bromination of polycyclic aromatic)
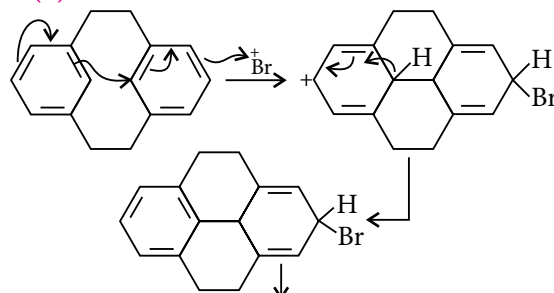
Can it tautomerise to give benzene back?
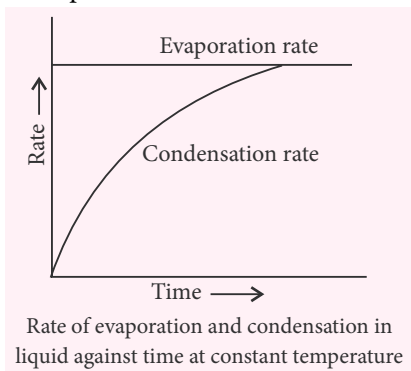Think if $-NO_2$ was there.
Yes, if $-NO_2$. But no if $-Br$.

ADVANCED CHEMISTRY BLOC

(VAPOUR PRESSURE AND SOLUBILITY OF GASES)

Mukul C. Ray, Odisha

Vapour Pressure

At constant temperature and surface area, the liquid begins to evaporate at a constant rate.

Rate of evaporation and condensation in liquid against time at constant temperature

The horizontal line in the graph represents this rate. The rate of condensation per unit area at constant temperature depends on the concentration of molecules in the vapour state. Slowly the rate of condensation increases and at one stage there is no further change in the vapour concentration with time. This maximum vapour exerts a pressure called vapour pressure.

Raoult's Law and Henry's Law

Statements of the laws are quite well known, hence are not discussed. It is better to consider both the laws together. A book writes, "An ideal solution is that where each component follows Raoult's law in the entire range of concentration and an ideally-dilute solution is that where the solute follows the Henry's law and the solvent the Raoult's law". What does it mean exactly? When the component is nearly pure (the solvent), it behaves according to Raoult's law and has a vapour pressure that is proportional to its mole fraction with proportionality constant that is vapour pressure of the pure substance, $p°$. When it is the minor component (the solute), its vapour pressure is still proportional to its mole fraction, but the constant of proportionality is now Henry's law constant, K_H.
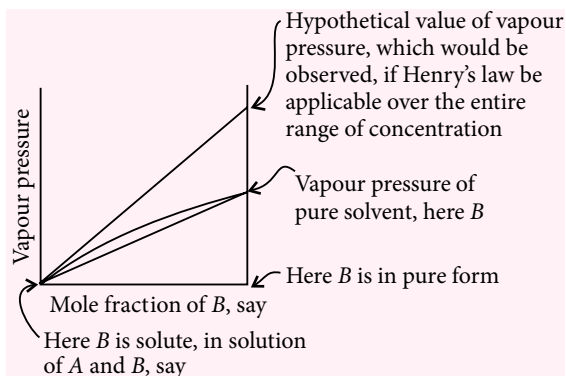

Diagram showing the vapour pressure dependence on mole fraction. At extreme left, the solution follows Henry's law and at the extreme right, it follows Raoult's law and no laws in between.

A quantitative explanation why the solvent should obey Raoult's law and the solute the Henry's law when they are together is as follows. In a very dilute solution, the solvent molecules are surrounded by other solvent molecules and they behave as they are in the pure form. However, the solute molecules are surrounded by solvent molecules only and therefore their properties are not the same as in the pure liquid or solid.

Two types of Henrian behaviour have been noticed. The one in which the Henry law constant is larger than pure vapour pressure and the Henry law constant line lies above the Raoult's line (as shown in the diagram, example alcohol-water mixture) and the other where the Henry's law line lies below

the Raoult's line (not shown in diagram, example chloroform-acetone mixture). In this context Raoult's law may be considered as a special case of Henry's law where Henry's law constant and pure vapour pressure have equal values.

Note: Ideal solution hardly exists but ideally dilute solutions do.

Solubility of Gases and Henry's Law Constant

For a more soluble gas, Henry's law constant is lower.

The solubility of most non-polar gases in water goes through a minimum as temperature increases. Solubility of gases in water is always an exothermic process but this is not true for salts. For example, dissolution of sodium chloride is endothermic. When a solute dissolves in water, energy is required to take the solute and solvent to expanded form and then energy is released when solute and solvent interact. Depending on the relative amount of heat required and released the process is either exothermic or endothermic. In case of gas energy is not required to take it to expanded form or to break its forces of attraction. So the process has always more energy to release.

Diagram showing variation of Henry's law constant in water with temperature.
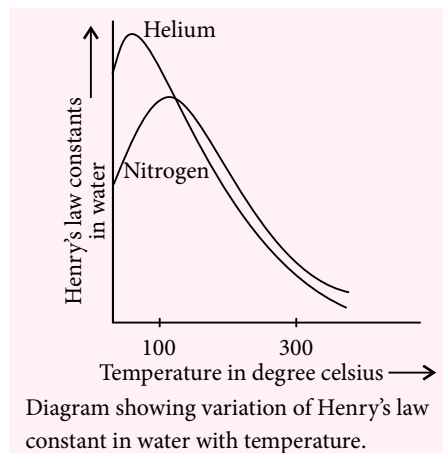
But solubility of gases in water increases strongly as the critical temperature of water (374°C) is approached. At critical temperature water is a poor dielectric, a bad solvent for electrolytes and prefers to mix non-polar gases and organic molecules. The anomalous property of water is due to hydrogen bonding that nearly does not exist at around critical temperature.

Henry's Law and Breathing

During inspiration the chest expands and pressure inside the lungs decreases relative to atmospheric pressure. During expiration, the chest contracts and the pressure becomes more inside the lungs. Alveolar gas is a mixture of newly inhaled air and air to be exhaled. The concentration of oxygen in arterial blood is equivalent to a partial pressure of about 40 torr, whereas the partial pressure of oxygen in freshly inhaled air is about 104 torr. The blood takes just about 0.75 sec to pass through the alveolus. But the high-pressure gradient helps blood to get saturated with oxygen within this short span. For carbon dioxide the pressure gradient is much less. Since carbon dioxide is much more soluble in alveolar fluid than oxygen; equal amounts of oxygen and carbon dioxide are exchanged during each breathe.

Does 'PRANAYAM' really help?

Possibly 'Yes'. By deep breathing constantly for a couple of minutes, blood gets fully saturated with oxygen. Not only that all the carbon dioxide produced in the cells due to combustion reactions is now forcefully exhaled. Such high amount of oxygen may even act as an antioxidant killing the unnecessary radicals in the body. It also ensures modest increase in body's intrinsic quantities of health promoting antioxidants.

The Lake Nyos Tragedy and Henry's Law

On August 21, 1986, a cloud of gas suddenly boiled from Lake Nyos in Cameroon killing nearly 2000 people. It is a deep lake. Layers of warm, less denser water float on the colder, denser water layers near the lake's bottom. Under normal conditions the lake stays in this way with very little mixing between the layers. It is believed that carbon dioxide gas had seeped into the cold water at the lake's bottom and dissolved in great amounts over hundreds of years due to high partial pressure of carbon dioxide, a clear application of Henry's law. For some reason, possibly due to unusual cooling of the lake's surface owing to monsoon clouds, the lake apparently suffered an overturn releasing massive quantities of gaseous carbon dioxide and suffocating humans and animals.

∞

Olympiad Problems for Practice

1. Low concentration of bromine, provided by NBS, favours substitution (allylic bromination) rather than addition of bromine on propene,

    $$CH_3CH\!=\!CH_2 \xrightarrow{\text{NBS}} BrCH_2CH\!=\!CH_2$$
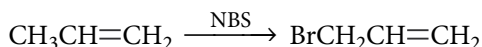
    This reaction is due to
    (a) reversibility of the following addition reaction,
    $$\overset{\bullet}{Br} + CH_3CH\!=\!CH_2 \rightleftharpoons CH_3\overset{\bullet}{C}HCH_2Br$$
    (b) irreversibility of the following substitution reaction,
    $$\overset{\bullet}{Br} + CH_3CH\!=\!CH_2 \longrightarrow Br\overset{\bullet}{C}HCH\!=\!CH_2$$
    (c) both of the above factors
    (d) none of the above factors.

2. Garnierite is a/an _____ ore.
    (a) oxide   (b) halide
    (c) silicate   (d) carbonate

3. Law of multiple proportion is followed by which of the following pairs?
    I. CH_4, C_2H_6 II. CO, CO_2
    III. NO, NO_2 IV. H_2O, H_2O_2
    (a) II and IV   (b) I, III and IV
    (c) I, II and IV   (d) All of these

4. The given compound exhibits x geometrical isomers and y optical isomers.

    $$\underset{H}{\overset{H_3C}{>}}C\!=\!C\underset{CH_2-CH_2-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3}{\overset{H}{<}}$$
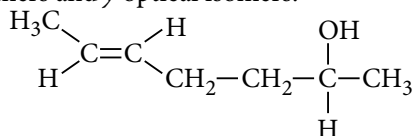
    The values of x and y are
    (a) 4 and 4   (b) 2 and 2
    (c) 2 and 4   (d) 4 and 2.

5. Which of the following statements is not true?
    (a) $[MnCl_4]^{2-}$ ion has tetrahedral geometry and is paramagnetic.

    (b) $[Mn(CN)_6]^{4-}$ ion has octahedral geometry and is diamagnetic.
    (c) $[CuCl_4]^{2-}$ ion has tetrahedral geometry and is paramagnetic.
    (d) $[Ni(Ph_3P)_2Br_3]$ has trigonal bipyramidal geometry and is paramagnetic.

6. If 10^{21} molecules are removed from 200 mg of CO_2, then the moles of CO_2 left are
    (a) 2.88×10^{-3} (b) 28.8×10^{-3}
    (c) 288×10^{-3} (d) 28.8×10^{3}

7. Identify A and B in the given reactions.
    $$B \xleftarrow{\text{KMnO}_4/\text{H}^+} (CH_3)_3COH \xrightarrow{\text{KMnO}_4/\text{OH}^-} A$$
    (a) A and B both are $(CH_3)_2C\!=\!CH_2$.
    (b) A and B, both are $(CH_3)_2CO + CH_2O$.
    (c) A is $(CH_3)_3COH$, while B is $(CH_3)_2C\!=\!CH_2$ or $(CH_3)_2CO$.
    (d) A and B, both are $(CH_3)_3COH$, as no reaction takes place.
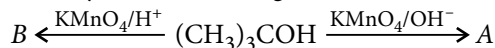
8. If 28 mL of 0.0032 M $Pb(NO_3)_2$ solution is added to 48 mL of 0.00012 M Na_2SO_4 solution then $(K_{sp(PbSO_4)} = 1.8 \times 10^{-8})$
    (a) $Q < K_{sp}$; precipitate will form
    (b) $Q > K_{sp}$; precipitate will form
    (c) $Q = K_{sp}$; precipitate will not form
    (d) precipitation does not depend upon Q and K_{sp} values.

9. At equilibrium, number of atoms disintegrating at two different stages are in the ratio of 1 : 10. If half-life of first stage is 15 minutes, half-life of second stage would be
    (a) 150 min   (b) 15 min
    (c) 1.5 min   (d) 30 min.

10. Three of the following four reactions are due to one similar feature of carbonyl compounds, while the fourth one is different. The fourth reaction is
(a) aldol condensation
(b) Knoevenagel reaction
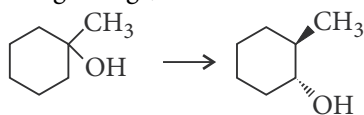(c) Wittig reaction
(d) haloform reaction.

11. Which two orbitals are located between the axes of coordinate system, and not along the axes?
(a) d_{xy}, d_{z^2} (b) d_{yz}, p_x
(c) $d_{x^2-y^2}, p_z$ (d) None of these

12. In transforming 0.01 mole of PbS to $PbSO_4$, the volume of '10 volume H_2O_2' required will be
(a) 11.2 mL   (b) 22.4 mL
(c) 33.6 mL   (d) 44.8 mL.

13. Provide a sequence of reactions to carry out the following change,

(a) $\xrightarrow[\Delta]{\text{conc. } H_2SO_4}$ $\xrightarrow[OH^-]{B_2H_6, H_2O_2}$

(b) $\xrightarrow[\Delta]{\text{conc. } H_2SO_4}$ $\xrightarrow{H_3O^+}$

(c) $\xrightarrow[\Delta]{\text{conc. } H_2SO_4}$ $\xrightarrow{Hg(OOCCH_3)_2}$

(d) $\xrightarrow[\Delta]{\text{conc. } H_2SO_4}$ $\xrightarrow{MnO_4^-, OH^-}$

14. Which of the following is not a true statement about FeO?
(a) It is non-stoichiometric and is metal deficient.
(b) It is basic oxide.
(c) Its aqueous solution changes to $Fe(OH)_3$ and then to $Fe_2O_3 \cdot (H_2O)_n$ by atmospheric oxygen.
(d) It gives red colour with KCNS.

15. At critical state, the compressibility factor (Z) for a real gas is equal to
(a) $\dfrac{3}{8}$ (b) $\dfrac{8}{3}$
(c) $\dfrac{4}{3}$ (d) $\dfrac{3}{4}$

16. Which one of the following does not belong to the same compound?
(a) Paraformaldehyde (b) Paraldehyde
(c) Trioxane   (d) Formalin

17. Which of the following is correct increasing order of hydrolysis?
(a) $CCl_4 < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$
(b) $PCl_5 < MgCl_2 < AlCl_3 < SiCl_4 < CCl_4$
(c) $PCl_5 < SiCl_4 < MgCl_2 < AlCl_3 < CCl_4$
(d) None of these

18. The number of H atoms, hybridisation of nitrogen atom and geometry around nitrogen in pyridine respectively are
(a) 4, sp^3, pyramidal
(b) 5, sp^2, planar
(c) 6, sp^2, planar
(d) 5, sp^2, pyramidal.

19. 15 mL of 0.20 M $MgCl_2$ solution is added to 45 mL of 0.40 M $AlCl_3$ solution. What is the molarity of Cl^-?
(a) 1.0 M   (b) 0.60 M
(c) 0.35 M   (d) 0.30 M

20. Which set is expected to show the smallest difference in first ionization energy?
(a) He, Ne, Ar   (b) B, N, O
(c) Mg, Mg^+, Mg^{2+} (d) Fe, Co, Ni

21. The decomposition of NH_3 on finely divided platinum is a first order reaction and follows the rate expression,
$$\text{Rate} = \frac{k_1[NH_3]}{1 + k_2[NH_3]}$$
only when concentration of NH_3 is
(a) very low   (b) very high
(c) moderate   (d) never followed.

22. Which of the following compounds does not dissolve in conc. H_2SO_4, even on warming?
(a) Ethylene   (b) Benzene
(c) Hexane   (d) Aniline

23. How many bonding pairs and lone pairs surround the central atom in I_3^- ion?
(a) 2 bonding pairs, 2 lone pairs
(b) 2 bonding pairs, 3 lone pairs
(c) 3 bonding pairs, 2 lone pairs
(d) 4 bonding pairs, 3 lone pairs

24. Two flasks *A* and *B* of equal volume containing 1 mole and 2 moles of O_3 respectively, are heated to the same temperature. When the reaction $2O_3 \rightleftharpoons 3O_2$ practically stops, then both the flasks shall have
  (a) the same ratio $[O_2]/[O_3]$
  (b) the same ratio $[O_2]^{3/2}/[O_3]$
  (c) only O_2
  (d) none of these.

25. Which of the following is not a sex hormone?
  (a) Testosterone   (b) Estrone
  (c) Estradiol   (d) Aldosterone

26. Asbestos has composition as
  (a) $CaO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$
  (b) $CaO \cdot 3MgO \cdot 4SiO_2$
  (c) $3MgO \cdot 4SiO_2 \cdot H_2O$
  (d) $Al_2O_3 \cdot SiO_2 \cdot 2H_2O$

27. Which of the following plots represents the behaviour of an ideal binary liquid solution?
  (a) Plot of p_{total} *vs* y_A is linear.
  (b) Plot of p_{total} *vs* y_B is linear.
  (c) Plot of $1/p_{total}$ *vs* y_A is linear.
  (d) Plot of $1/p_{total}$ *vs* y_B is non-linear.

28. Consider the following pairs of organic compounds and reagents :

Column I Pairs	Column II Reagents
(i) $CH_3COOH/HCOOH$	(*p*) Tollens'
(ii) CH_3CHO/CH_3COCH_3	(*q*) Fehling's
(iii) glucose/sucrose	(*r*) $NaOH/I_2$
(iv) glucose/fructose	

Which of the following is the correct match for distinction between the given pairs?
  (a) (i) - (*p*), (*q*); (ii) - (*p*), (*q*), (*r*); (iii) - (*p*), (*q*); (iv) - (*p*), (*q*)
  (b) (i) - (*p*), (*q*); (ii) - (*p*), (*q*); (iii) - (*p*), (*q*)
  (c) (i) - (*p*), (*q*), (*r*); (ii) - (*p*), (*q*); (iii) - (*p*), (*q*), (*r*); (iv) - (*p*)
  (d) (i) - (*p*), (*q*); (ii) - (*p*), (*q*); (iii) - (*p*); (iv) - (*q*)

29. Which of the following is a pair of paramagnetic species?

  (a) KO_2, NO_2 (b) K_2O_2, KO_2
  (c) K_2O, NO_2 (d) NO_2, N_2O_2

30. Which of the following solutions will have pH close to 1.0?
  (a) 100 mL of (M/10) HCl + 100 mL of (M/10) NaOH
  (b) 55 mL of (M/10) HCl + 45 mL of (M/10) NaOH
  (c) 10 mL of (M/10) HCl + 90 mL of (M/10) NaOH
  (d) 75 mL of (M/5) HCl + 25 mL of (M/5) NaOH

ANSWER KEYS

1. (c)	**2.** (c)	**3.** (d)	**4.** (b)	**5.** (b)
6. (a)	**7.** (c)	**8.** (b)	**9.** (a)	**10.** (c)
11. (d)	**12.** (d)	**13.** (a)	**14.** (d)	**15.** (a)
16. (b)	**17.** (a)	**18.** (b)	**19.** (a)	**20.** (d)
21. (c)	**22.** (c)	**23.** (b)	**24.** (b)	**25.** (d)
26. (b)	**27.** (c)	**28.** (b)	**29.** (a)	**30.** (d)

■■

SOLUTIONS TO FEBRUARY 2015 CROSSWORD
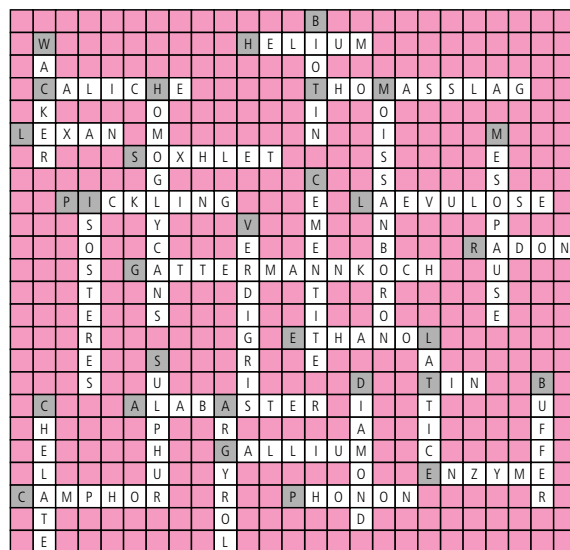
Winners of February 2015 Crossword

Seema Rawat (Delhi)

Dinesh Palia (Haryana)

**Kanika Sharma (Varanasi)**

Sender of January 2015 Crossword

Shubhneet Bhatia

CHEMISTRY MUSING

**1. (a) :** (I) $HClO_4$, in which chlorine exists in +7 (maximum) oxidation state does not undergo disproportionation.

(II) Molecules containing odd number of electrons are reactive and generally dimerise in order to pair the electrons, but ClO_2 is the exception.

Chlorine perchlorate, $Cl.ClO_4$ (Cl_2O_4) is made by the following reaction at –45°C.

$CsClO_4 + ClOSO_2F \longrightarrow Cs(SO_3)F + ClOClO_3$
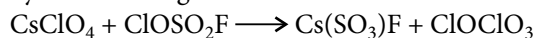
It is less stable than ClO_2, and decomposes to O_2, Cl_2 and Cl_2O_6 at room temperature.

(III) Structure of Cl_2O_7 :

O O O
\|171 pm \|141 pm \|
Cl——O——Cl
119° 115°
O O O
O

(IV) $Rb[ICl_2] \xrightarrow{\Delta} RbCl + ICl$
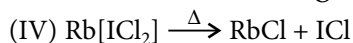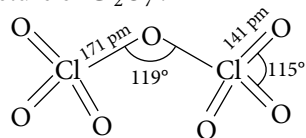
2. (d) : Volume strength = 5.6 × Normality

$$N_1 = \frac{10}{5.6}; \ N_2 = \frac{15}{5.6}; \ N_3 = \frac{20}{5.6}$$

$$N_1V_1 + N_2V_2 + N_3V_3 = N_RV_R$$

$$\Rightarrow \frac{10}{5.6}\times\frac{1}{2} + \frac{15}{5.6}\times\frac{1}{2} + \frac{20}{5.6}\times\frac{1}{2} = N_R \times 3$$

$$\Rightarrow N_R = 1.339$$

∴ Volume strength of resultant solution
$= N_R \times 5.6 = 1.339 \times 5.6 = 7.5$

3. (c) : $P = p_A^{\circ} x_A + p_B^{\circ} x_B$ (from Raoult's law)

Case I.
$550 = p_A^{\circ} \times [1/(1 + 3)] + p_B^{\circ} \times [3/(1 + 3)]$ ...(i)

Case II. On adding one mole of B in liquid mixture,

$560 = p_A^{\circ} \times [1/(1 + 4)] + p_B^{\circ} \times [4/(1 + 4)]$ ...(ii)

Solving (i) and (ii), we get

$p_A^{\circ} = 400$ mm of Hg
$p_B^{\circ} = 600$ mm of Hg

4. (c) : Reaction of salicylic acid with Br_2/H_2O gives white ppt. of 2, 4, 6-tribromophenol.

The reaction involves bromination with decarboxylation.

OH OH OH
\|COOH \| Br\|Br
Salicylic $\xrightarrow[-CO_2]{Br_2}$ Phenol $\xrightarrow{Br_2}$
acid Br

2, 4, 6-Tribromophenol
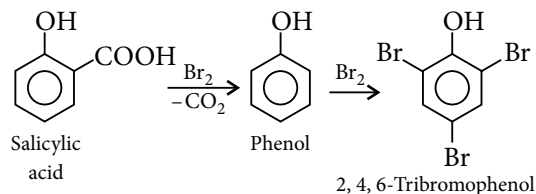
5. (b)   **6. (c)**   **7. (c)**

8. (d) : $\left(P + \dfrac{an^2}{V^2}\right)(V - nb) = nRT$

(for n moles of a gas)

or $\quad a = \left(\dfrac{nRT}{V - nb} - P\right)\dfrac{V^2}{n^2}$

$$a = \left(\frac{3 \times 0.082 \times 373}{6 - 3 \times 0.05} - 13\right)\frac{(6)^2}{(3)^2}$$

$$= \left(\frac{91.758}{5.85} - 13\right)\frac{36}{9}$$

$$= (2.685) \times 4 = 10.74 \text{ atm L}^2 \text{ mol}^{-2}$$

9. (3) :

O
\|\|
$Cl-C-OC_2H_5 + RMgX \longrightarrow$
Ethyl chloroformate

O OMgX
\|\| \|
$R-C-OC_2H_5 \xleftarrow[(-ClMgX)]{} Cl-C-OC_2H_5$
\|
R

$\Big\downarrow RMgX$

OMgX
\|
$R-C-OC_2H_5 \xrightarrow[(-XMgOC_2H_5)]{}$
\|
R

O
\|\|
$R-C-R$

$\Big\downarrow RMgX$

OH OMgX
\| \|
$R-C-R \xleftarrow{H_2O/H^+} R-C-R$
\| \|
R R

(3° alcohol)

10. (7) : $(CH_3)_2CHN = NCH(CH_3)_{2(g)} \longrightarrow$
$\qquad\qquad\qquad N_{2(g)} + C_6H_{14(g)}$
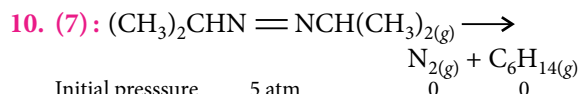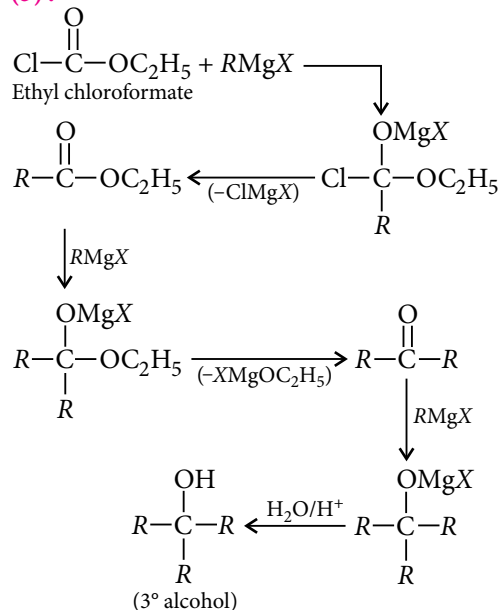
Initial pressure	5 atm	0	0
After 1 hour	$5 - \dfrac{40}{100} \times 5$	2 atm	2 atm
	$= 5 - 2 = 3$ atm		

Total pressure after one hour = 3 + 2 + 2
$\qquad\qquad\qquad\qquad\qquad = 7$ atm
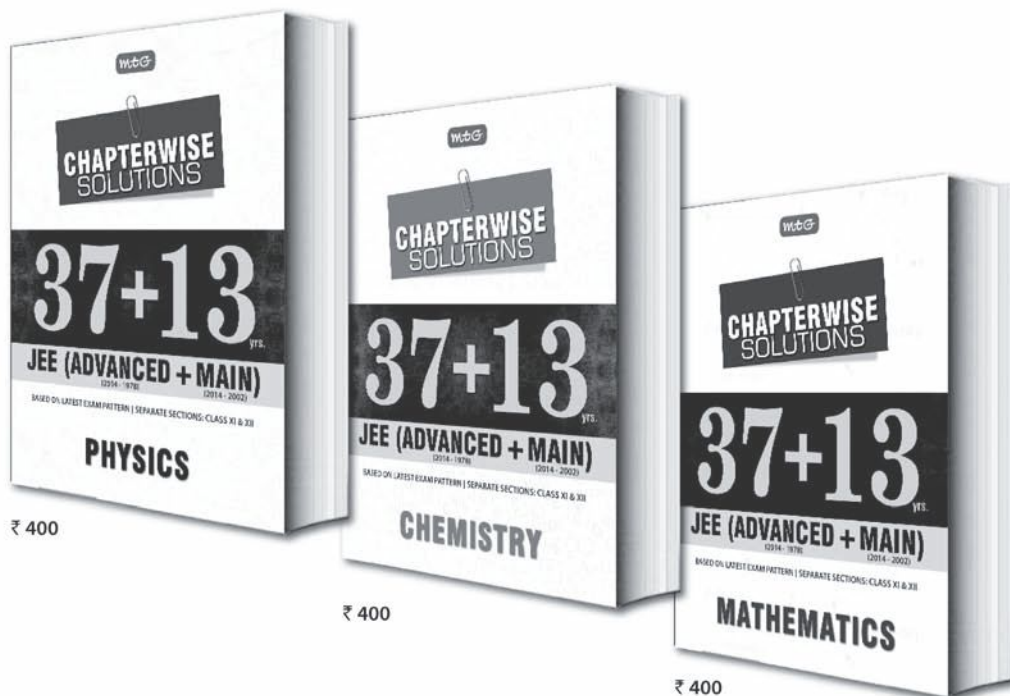
ASSERTION & REASON

Directions : Mark the correct choice as:

(a) If both assertion and reason are true and reason is the correct explanation of assertion.

(b) If both assertion and reason are true but reason is not the correct explanation of assertion.

(c) If assertion is true but reason is false.

(d) If both assertion and reason are false.

PHYSICAL CHEMISTRY

1. **Assertion :** Camphor is used as solvent in the determination of molecular masses of naphthalene, anthracene, etc.
   Reason : Camphor has high molal elevation constant.

2. **Assertion :** For a reaction, $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ if the volume of vessel is reduced to half of its original volume, equilibrium constant will be doubled.
   Reason : According to law of equilibrium, reaction shifts in a direction that tends to undo the effect of the stress.

3. **Assertion :** Most probable velocity is the velocity possessed by maximum fraction of molecules at the same temperature.
   Reason : On collision, more and more molecules acquire higher speed at the same temperature.

4. **Assertion :** B_2H_6, Si_2H_6 are said to have similar structures.
   Reason : They have same number of σ and π bonds.

5. **Assertion :** Stannous chloride gives grey precipitate with mercuric chloride, but stannic chloride does not do so.
   Reason : Stannous chloride is a powerful oxidising agent which oxidises mercuric chloride to metallic mercury.

6. **Assertion :** A spectral line will be observed for a $2p_x – 2p_y$ transition.
   Reason : The energy is released in the form of wave of light when electron drops from $2p_x$ to $2p_y$ orbital.

7. **Assertion :** Compressibility factor for hydrogen varies with pressure with positive slope at all pressures.
   Reason : Even at low pressures, repulsive forces dominate for hydrogen gas.

8. **Assertion :** Gases like N_2, O_2 behave as ideal gas at low temperature and high pressure.
   Reason : Strong molecular interactions are responsible for ideal behaviour.

9. **Assertion :** Number of gram molecules of SO_2Cl_2 in 13.5 g of sulphuryl chloride is 0.2.
   Reason : Gram molecule is equal to those molecules which are expressed in gram.

10. **Assertion :** In crystal lattice, the size of the cation is larger in a tetrahedral hole than in an octahedral hole.
    Reason : The cations occupy more space than atoms in crystal packing.

ORGANIC CHEMISTRY

11. **Assertion :** Cycloheptatrienyl cation is aromatic.
    Reason : Aromatic molecules have high degree of thermodynamic stability.

12. Assertion : Nitroethane ($C_2H_5NO_2$) shows functional isomerism as well as tautomerism.

Reason : Nitroethane shows tautomerism due to presence of α-hydrogens and it has same molecular formula as that of ethyl nitrite.

13. Assertion : Oxidation of toluene with chromic oxide to get benzaldehyde is carried out in the presence of acetic anhydride.

Reason : Presence of methyl group in toluene activates benzene ring towards electrophilic substitution reactions.

14. Assertion : $(CH_3)_3CCOC(CH_3)_3$ and acetone can be distinguished by the reaction with $NaHSO_3$.

Reason : HSO_3^- is the nucleophile in bisulphite addition.

15. Assertion : *t*-Butyl methyl ether is not prepared by the reaction of *t*-butyl bromide with sodium methoxide.

Reason : Sodium methoxide is a strong nucleophile.

16. Assertion : 2-Chloro-3-methylbutane on treatment with alcoholic potash gives 2-methylbut-2-ene as major product.

Reason : The reaction occurs according to Saytzeff rule.

17. Assertion : Sulphanilic acid exists as dipolar ion whereas *p*-aminobenzoic acid does not.

Reason : Carboxyl group being more acidic than $-SO_3H$ group can easily transfer a proton to the amino group.

18. Assertion : Isobutane on oxidation with $KMnO_4$ gives *tert*-butyl alcohol.

Reason : Oxidising agents have no effect on alkanes.

19. Assertion : All carbon atoms in but-1, 3-diene are sp^2 hybridized.

Reason : 1, 3-butadiene is a conjugated diene.

20. Assertion : Enol form of cyclohexane-1, 3, 5-trione is more stable than its keto form.

Reason : Enol form contains α-hydrogen atoms.

INORGANIC CHEMISTRY

21. Assertion : NO_3^- is planar while NH_3 is pyramidal.

Reason : N in NO_3^- is sp^2 hybridized but in NH_3 it is sp^3-hybridized.

22. Assertion : In fused state, $CaCl_2$ cannot be used to dry alcohol or ammonia.

Reason : $CaCl_2$ is not a good dessicant.

23. Assertion : Potassium ferrocyanide is diamagnetic whereas potassium ferricyanide is paramagnetic.

Reason : Crystal field splitting in ferrocyanide ion is greater than that of ferricyanide ion.

24. Assertion : The oxidation number of platinum in Zeise's salt is +2.

Reason : C_2H_4 ligand carries -2 charge.

25. Assertion : $HClO_4$ is a stronger acid than $HClO_3$.

Reason : Oxidation state of Cl in $HClO_4$ is VII and in $HClO_3$ is V.

26. Assertion : Reaction of conc. H_2SO_4 on NaBr and NaI does not give HBr and HI.

Reason : HBr and HI are oxidised by conc. H_2SO_4 to Br_2 and I_2.

27. Assertion : Wolframite impurities are separated from cassiterite by electromagnetic separation.

Reason : Cassiterite being magnetic is attracted by the magnet and forms a separate heap.

28. Assertion : $[Al(H_2O)_6]^{3+}$ is a stronger acid than $[Mg(H_2O)_6]^{2+}$.

Reason : Size of $[Al(H_2O)_6]^{3+}$ is smaller than $[Mg(H_2O)_6]^{2+}$ and possesses more effective nuclear charge.

29. Assertion : Saline hydrides are non-volatile, non-conducting and crystalline solids.

Reason : Saline hydrides are compounds of hydrogen with most of the *p*-block elements.

30. Assertion : Mohr's salt is used as a primary standard in volumetric analysis.

Reason : Mohr's salt contains both Fe^{2+} and Fe^{3+} ions in the crystalline salt.

SOLUTIONS

**1. (c) :** Camphor has high molal depression constant.

2. (d) : There is no change in number of gas molecules. Therefore the expression for *K* is independent of volume. Hence *K* will remain same.

According to Le-Chatelier's principle, reaction shifts in a direction that tends to undo the effect of stress.

3. (c) : On collision, some molecules are speeded up while others are slowed down.

4. (d) : B_2H_6 is an electron deficient compound. B_2H_6 contains some unusual bonds which are called as 3-centre-2-electron bonds.

banana bonds
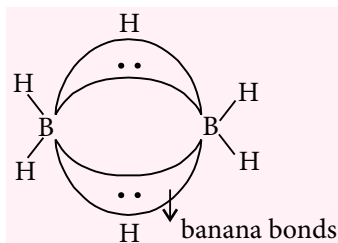
Si_2H_6 is called disilane.

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{Si}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{Si}}-H$$
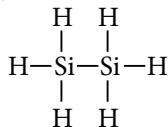
5. (c) : $SnCl_2$ (stannous chloride) on reaction with mercuric chloride ($HgCl_2$), gets oxidised to $SnCl_4$ (stannic chloride)

$SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + Hg_2Cl_2$
(Greyish)

$SnCl_2 + Hg_2Cl_2 \rightarrow 2Hg + SnCl_4$
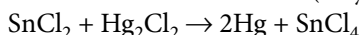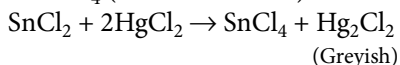
So in this reaction, stannous chloride is acting as reducing agent that reduces Hg(II) to Hg(I) and then to Hg(0).

6. (d) : $2p_x$ and $2p_y$ orbitals are degenerate orbitals, *i.e.*, they are of equal energy and hence there is no possibility of transition of electron.

7. (a) : In case of H_2, compressibility factor increases with the pressure. At 273 K, $Z > 1$ which shows that it is difficult to compress the gas as compared to ideal gas. In this case, repulsive forces dominate.

8. (d) : N_2, O_2 and other common gases behave as ideal gas at low pressure and high temperature. Under these conditions molecular interactions are negligible and thus obey Boyle's law, Charles law and kinetic theory of gases.

9. (d) : No. of gram molecules or mole molecules

$= \dfrac{\text{wt. of sub.}}{\text{GMM}}$ (GMM = Gram Molecular Mass)

∴ GMM of SO_2Cl_2 = 135 g

Hence number of gram molecules $= \dfrac{13.5}{135} = 0.1$

10. (d) : Tetrahedral holes are smaller than octahedral holes.

Cations are smaller in size than corresponding atoms.

11. (b) : Cycloheptatrienyl cation is planar and has delocalized six π-electrons, hence it follows $(4n + 2)$π-electrons rule so it is aromatic.

12. (a) : Tautomers:

Functional isomers:

$CH_3-CH_2-NO_2$ and $CH_3-CH_2-O-N=O$
Nitroethane   Ethyl nitrite
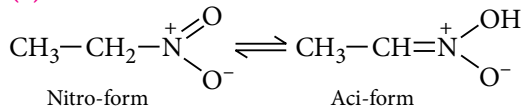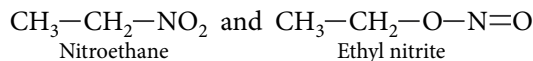
13. (b) : Oxidation of toluene with chromic oxide gives benzaldehyde which reacts with acetic anhydride to give benzylidene diacetate and thus further oxidation of benzaldehyde to benzoic acid is checked by acetic anhydride. The benzylidene diacetate on treatment with HCl regenerates benzaldehyde.
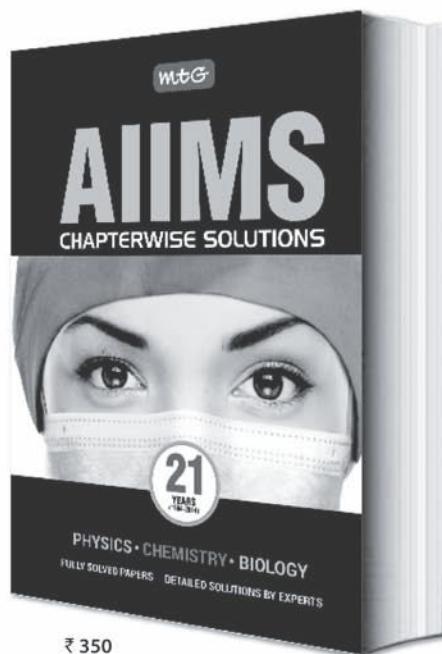
14. (b) : HSO_3^- is a bulky nucleophile, hence, cannot attack on sterically hindered ketones.

15. (b) : In Williamson's synthesis, if a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed.

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br + NaOCH_3 \longrightarrow$$

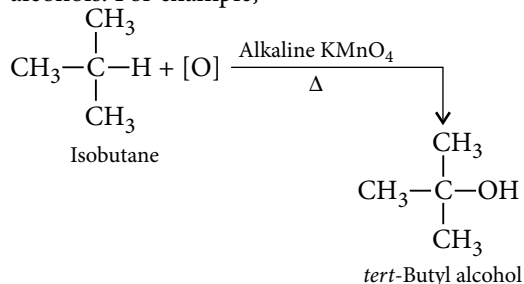$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + NaBr$$

2-Methylpropene
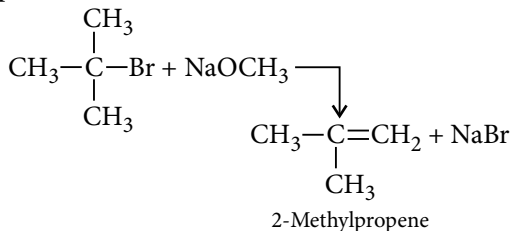
It is because alkoxides are not only nucleophiles but also strong bases as well. They react with alkyl halides leading to elimination reaction.

16. (a) : 2-Chloro-3-methylbutane on treatment with alcoholic potash gives 2-methylbut-2-ene as main product.

$$H_3C-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}-CH_3 \xrightarrow{\text{alc. KOH}}$$

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3 + CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$$

Major   Minor
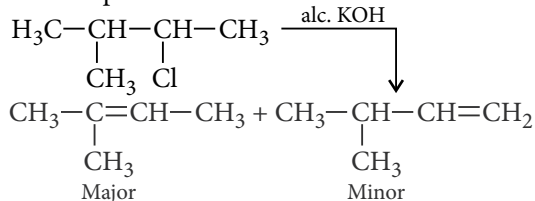
Elimination occurs according to Saytzeff rule, "the major product is one which involves elimination of H from less hydrogenated carbon".

17. (c) : $-SO_3H$ group being more acidic than $-CO_2H$ group can easily transfer a proton to the amino group.

18. (c) : Normally oxidising agents have no effect on alkanes. However, alkanes containing a tertiary hydrogen atom can be oxidised by oxidising agents such as $KMnO_4$ to the corresponding alcohols. For example,

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-H + [O] \xrightarrow[\Delta]{\text{Alkaline } KMnO_4}$$

Isobutane

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

tert-Butyl alcohol

19. (b) : In 1, 3-butadiene, all the carbon atoms form 3 σ bonds, so they are sp^2 hybridised.

20. (b) : Enol form of cyclohexane-1, 3, 5-trione is stabilized by resonance.

21. (a)

22. (c) : $CaCl_2$ forms addition products with ammonia or alcohol.

23. (c) : $[Fe(CN)_6]^{4-}$
Diamagnetic
d^2sp^3 hybridisation

$[Fe(CN)_6]^{3-}$
Paramagnetic
d^2sp^3 hybridisation
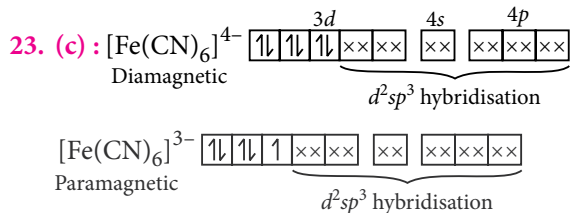
In ferrocyanide ion, the oxidation state of Fe is +2 however, in ferricyanide ion, the oxidation state of Fe is +3.

Generally, the higher the oxidation state of the metal, the greater is the crystal field splitting. It means crystal field splitting in ferrocyanide ion is lower than that of ferricyanide ion.

24. (c) : In Zeise's salt $K[PtCl_3(\eta^2-C_2H_4)]$, C_2H_4 is a neutral ligand.

25. (b) : Acidic strength increases as oxidation number of the halogen in the acid increases. This is explained on the basis of relative stability of the anion or the conjugate base formed after removal of a proton. As ClO_4^- is more stable than ClO_3^- due to greater dispersal of negative charge on four oxygen atoms hence, $HClO_4$ is a stronger acid than $HClO_3$.

26. (a) : Conc. H_2SO_4 is a strong oxidising agent.

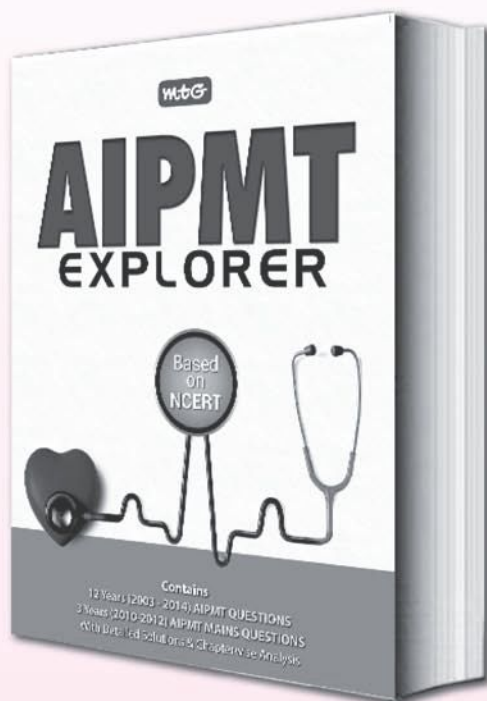**27. (c) :** Wolframite being magnetic is attracted by the magnetic roller and forms a heap under it.

28. (a) : The size of $[Al(H_2O)_6]^{3+}$ is smaller than $[Mg(H_2O)_6]^{2+}$. Also the former possesses more effective nuclear charge and thus attracts electron pair from donor more effectively. This gives rise to relatively strong acidic nature of $[Al(H_2O)_6]^{3+}$.

29. (c) : Saline or ionic hydrides are compounds of hydrogen with most of the *s*-block elements. However, with *p*-block elements hydrogen forms molecular or covalent hydrides.

30. (c) : Mohr's salt contains only Fe^{2+} ions without any trace of Fe^{3+} ions. Thus a standard solution of Fe^{2+} ions can be obtained directly by weighing a known amount of the Mohr's salt.

■■

80. (b) : Given differential equation is

$$\cos\left(\frac{dy}{dx}\right) = a \implies \frac{dy}{dx} = \cos^{-1} a$$

$$\implies dy = \cos^{-1} a\, dx$$

On integrating both sides, we get

$$\int dy = \int \cos^{-1} a\, dx \implies y = x \cos^{-1} a + C \quad …(i)$$

When $x = 0$ and $y = 2$

$$\therefore \quad 2 = 0 + C \implies C = 2$$

Now, (i) becomes $y = x \cos^{-1} a + 2$

81. (c) : Let merchant has stock of desktop model x units and portable model y units.

Total profit to maximize $z = 4500x + 5000y$

Subject to constraints

$$x + y \le 250$$
$$25000x + 40000y \le 7000000$$
or $5x + 8y \le 1400$
and $x \ge 0, y \ge 0$

Now, draw the graph of $x + y = 50$ and $5x + 8y = 1400$ we get, the feasible region *OAECO*. The corner points of the feasible region are $O(0, 0)$, $A(250, 0)$, $E(200, 50)$ and $C(0, 175)$
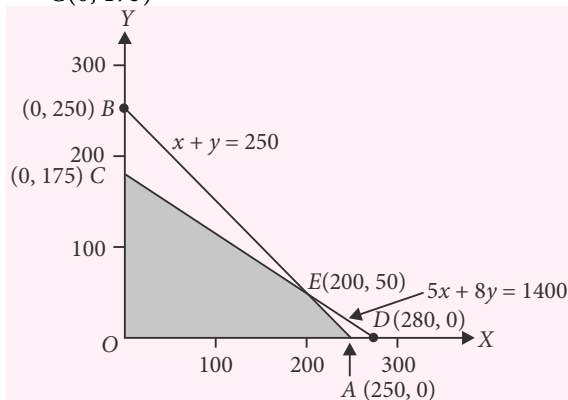
The value of $z = 4500x + 5000y$

At $A(250, 0)$, $z = 4500 \times 250 + 5000 \times 0$
$$= 1125000$$

At $E(200, 50)$, $z = 4500 \times 200 + 5000 \times 50$
$$= 1150000$$

At $C(0, 175)$, $z = 4500 \times 0 + 5000 \times 175$
$$= 875000$$

At $O(0, 0)$, $z = 0$

Clearly, maximum profit is ₹ 1150000 at $E(200, 50)$ *i.e.*, when 200 desktops and 50 portable models are in stock.

82. (d) : We are given that two parabolas $y^2 = 4ax$ and $x^2 = 4ay$. Solving eq. of these parabolas, we get

$$\left(\frac{x^2}{4a}\right)^2 = 4ax \qquad [\because y^2 = 4ax]$$

$$\implies x^4 = 64a^3 x$$
$$\implies x(x^3 - 64a^3) = 0 \implies x = 0, 4a$$

When $x = 0$, then $y = 0$

When $x = 4a$, then $y = 4a$

$\therefore$ Points of intersection are $(0, 0)$ and $(4a, 4a)$
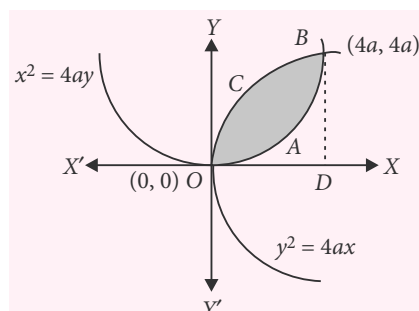
$\therefore$ Area of the shaded region

= Area of region *ODBCO* – Area of region *ODBAO*

$$= 2\sqrt{a}\left[\frac{x^{3/2}}{3/2}\right]_0^{4a} - \frac{1}{4a}\left[\frac{x^3}{3}\right]_0^{4a}$$

$$= 2\sqrt{a}\,\frac{(4a)^{3/2}}{3/2} - \frac{1}{4a}\left[\frac{64a^3}{3}\right]$$

$$= \frac{4}{3} \times 8a^2 - \frac{16a^2}{3} = \frac{32a^2}{3} - \frac{16a^2}{3} = \frac{16a^2}{3} \text{ sq. units}$$

83. (d) : Given that, plane passing through the point $(1, 1, 1)$ and containing the line

$$\vec{r} = (-3\hat{i} + \hat{j} + 5\hat{k}) + \lambda(3\hat{i} - \hat{j} - 5\hat{k})$$

Therefore, equation of the required plane is

$$\begin{vmatrix} x - x_1 & y - y_1 & z - z_1 \\ x_2 - x_1 & y_2 - y_1 & z_2 - z_1 \\ a & b & c \end{vmatrix} = 0$$

Consider $(x_1, y_1, z_1) = (1, 1, 1)$,
$(x_2, y_2, z_2) = (-3, 1, 5)$ and $(a, b, c) = (3, -1, -5)$

$$\therefore \quad \begin{vmatrix} x - 1 & y - 1 & z - 1 \\ -4 & 0 & 4 \\ 3 & -1 & -5 \end{vmatrix} = 0$$

$$\implies x - 2y + z = 0$$

84. (b) : $|x - 3|^{(x^2 - 8x + 15)/(x-2)} = 1$

$\Rightarrow x \neq 3, x \neq 2$ and $\dfrac{x^2 - 8x + 15}{x-2} \log|x-3| = 0$

$\Rightarrow x \neq 2, x \neq 3$ and $|x - 3| = 1$ or $x^2 - 8x + 15 = 0$

$\Rightarrow x \neq 2, x \neq 3$ and $[x = 2$ or 4 or $(x-3)(x-5) = 0]$

$\Rightarrow x = 4$ or $x = 5$

Therefore, the number of the solutions of the given equation is 2.

85. (a) : We know that

$\dfrac{x-y}{x+y} = \dfrac{(\cos\alpha - \cos\beta) + i(\sin\alpha - \sin\beta)}{(\cos\alpha + \cos\beta) + i(\sin\alpha + \sin\beta)}$

$= \dfrac{\begin{array}{c} -2\sin[(\alpha+\beta)/2]\sin[(\alpha-\beta)/2] \\ +2i\cos[(\alpha+\beta)/2]\sin[(\alpha-\beta)/2] \end{array}}{\begin{array}{c} 2\cos[(\alpha+\beta)/2]\cos[(\alpha-\beta)/2] \\ +2i\sin[(\alpha+\beta)/2]\cos[(\alpha-\beta)/2] \end{array}}$

$= \dfrac{i\sin[(\alpha-\beta)/2]\{\cos[(\alpha+\beta)/2] + i\sin[(\alpha+\beta)/2]\}}{\cos[(\alpha-\beta)/2]\{\cos[(\alpha+\beta)/2] + i\sin[(\alpha+\beta)/2]\}}$

$= i\tan\left(\dfrac{\alpha - \beta}{2}\right)$

86. (b) : Let the observations be $x_1, x_2, ..., x_{20}$ and $\overline{x}$ be their mean. Given that, variance = 5 and $n = 20$. We know that,

$$\text{Variance } (\sigma^2) = \dfrac{1}{n}\sum_{i=1}^{20}(x_i - \overline{x})^2$$

i.e., $5 = \dfrac{1}{20}\sum_{i=1}^{20}(x_i - \overline{x})^2$ or $\sum_{i=1}^{20}(x_i - \overline{x})^2 = 100$ ...(i)

If each observation is multiplied by 2 and the new resulting observations are y_i, then

$$y_i = 2x_i \text{ i.e., } x_i = \dfrac{1}{2}y_i$$

Therefore, $\overline{y} = \dfrac{1}{n}\sum_{i=1}^{20}y_i = \dfrac{1}{20}\sum_{i=1}^{20}2x_i = 2\cdot\dfrac{1}{20}\sum_{i=1}^{20}x_i$

i.e., $\overline{y} = 2\overline{x}$ or $\overline{x} = \dfrac{1}{2}\overline{y}$

On substituting the values of x_i and $\overline{x}$ in (i), we get

$$\sum_{i=1}^{20}\left(\dfrac{1}{2}y_i - \dfrac{1}{2}\overline{y}\right)^2 = 100 \Rightarrow \sum_{i=1}^{20}(y_i - \overline{y})^2 = 400$$

Thus, the variance of new obsevations

$$= \dfrac{1}{20}\times 400 = 20 = 2^2 \times 5$$

87. (a) : $\sim p$: there exists atleast one positive real number x for which $(x - 1)$ is not positive.

88. (c) : Let the statement $P(n)$ be defined as

$$P(n): \left(1+\dfrac{3}{1}\right)\left(1+\dfrac{5}{4}\right)\left(1+\dfrac{7}{9}\right)...\left(1+\dfrac{(2n+1)}{n^2}\right)$$
$$= (n+1)^2$$

Step I: For $n = 1$,

i.e., $P(1): \left(1+\dfrac{3}{1}\right) = (1+1)^2 \Rightarrow 4 = 4$

Hence, $P(1)$ is true.

Step II: Let it is true for $n = k$,

i.e., $\left(1+\dfrac{3}{1}\right)\left(1+\dfrac{5}{4}\right)\left(1+\dfrac{7}{9}\right)...\left(1+\dfrac{2k+1}{k^2}\right)$
$$= (k+1)^2 \qquad ...(i)$$

Step III: For $n = k + 1$,

$\left\{\left(1+\dfrac{3}{1}\right)\left(1+\dfrac{5}{4}\right)\left(1+\dfrac{7}{9}\right)...\left(1+\dfrac{2k+1}{k^2}\right)\right\}$
$$\left(1+\dfrac{2k+2+1}{(k+1)^2}\right)$$

$= (k+1)^2\left(1+\dfrac{2k+3}{(k+1)^2}\right) \qquad$ [using (i)]

$= (k+1)^2\left[\dfrac{(k+1)^2 + 2k+3}{(k+1)^2}\right]$

$= k^2 + 2k + 1 + 2k + 3 = (k+2)^2 = [(k+1)+1]^2$

Therefore, $P(k + 1)$ is true when $P(k)$ is true. Hence, from the principle of mathematical induction, the statement is true for all natural numbers n.

89. (a)

90. (a) : We have, $y = \sin^{-1} x$

On differentiating both sides w.r.t. x, we get

$$\dfrac{dy}{dx} = \dfrac{1}{\sqrt{1-x^2}} \Rightarrow \sqrt{1-x^2}\,\dfrac{dy}{dx} = 1$$

Again, differentiating both sides w.r.t. x, we get

$$\sqrt{1-x^2}\,\dfrac{d^2y}{dx^2} + \dfrac{dy}{dx}\times\dfrac{1}{2\sqrt{1-x^2}}(-2x) = 0$$

$$\Rightarrow \dfrac{\left[(1-x^2)\dfrac{d^2y}{dx^2} - x\dfrac{dy}{dx}\right]}{\sqrt{1-x^2}} = 0$$

$$\Rightarrow (1-x^2)\dfrac{d^2y}{dx^2} - x\dfrac{dy}{dx} = 0$$

Y?U ASKED WE ANSWERED

**Do you have a question that you just can't get answered?**

Use the vast expertise of our mtg team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough.

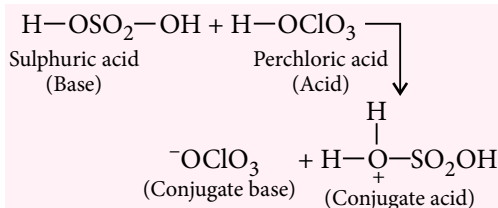The best questions and their solutions will be printed in this column each month.

Q1. Why perchloric acid is stronger acid than sulphuric acid, though it is considered as 'king of acids'?
–Parth Savaliya and Suraj Gohel, Rajkot (Gujarat)

Ans. The structures of these oxo-acids are

Sulphuric acid and Perchloric acid
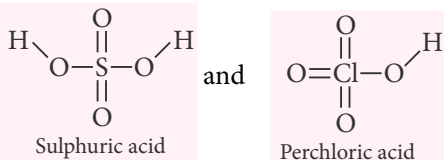
Cl atom is smaller in size and more electronegative as compared to S atom. It will tend to attract the shared pair of electrons more towards itself. This will create high polarity in O—H bond thereby allowing the proton to dissociate and make the compound acidic. Also, ClO_4^- ion has greater resonance stability than HSO_4^- ion. Thus, H_2SO_4 is a weaker acid than $HClO_4$ and acts as a base to accept proton from $HClO_4$.

$$H-OSO_2-OH + H-OClO_3 \longrightarrow$$
Sulphuric acid (Base)   Perchloric acid (Acid)

$$^-OClO_3 + H-\overset{H}{\underset{+}{O}}-SO_2OH$$
(Conjugate base)   (Conjugate acid)

Q2. We know the compound PF_5 exists, but why PH_5 doesn't? *–Alapan Kar, Nadia (W.B.)*

Ans. The valence bond explanation is

Five unpaired electrons in outer shell
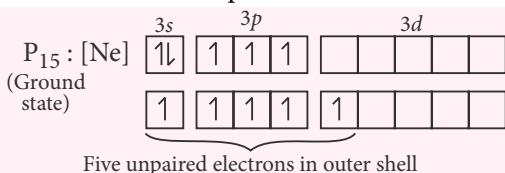
This excitation will take place only when the 'orbital contraction' occurs which is possible by attaching more electronegative atom (F) to the central atom. Hydrogen is not so electronegative to contract the *d*-orbital sufficiently so that it may be used for bonding.

Q3. According to Hückel's rule, "any cyclic, planar and conjugated compound containing $(4n + 2)\pi$ electrons is aromatic." So, how to recognize whether the structure is planar or not?
–Gawali Aishwarya Balasaheb, Pune (M.H.)

Ans. To find out whether the molecule is planar or not, the following factors are considered :

(i) Each atom in the ring must have an unhybridized *p*-orbital, forming *p*-orbital loop.

(ii) The unhybridized *p*-orbitals must overlap to form a continuous ring of parallel orbitals.

(iii) Delocalization of the π-electrons over the ring must lower the electronic energy.

Examples: **Benzene:** All the C-atoms are sp^2-hybridised. Each atom has a *p*-orbital, forming a loop and all orbitals lie in the same plane. Hence, it is a planar molecule.

Benzene (Aromatic, planar)
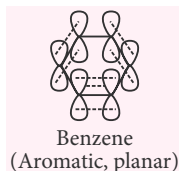
The molecules given below are non-planar due to the presence of sp^3-hybridized C-atom.

Cyclopropene (Non-aromatic, non-planar)

Cyclopentadiene (Non-aromatic, non-planar)

Cycloheptatriene (Non-aromatic, non-planar)
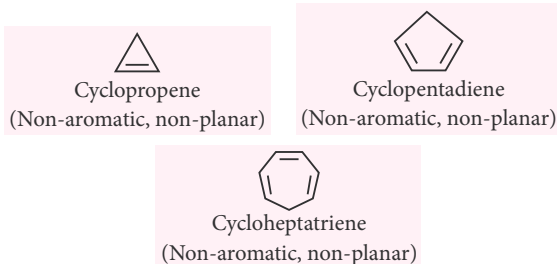
Cyclooctatetraene: It has the flexibility to adopt non-planar "tub" shaped conformation by abandoning its planar geometry which has ring strain. There is no continuous overlapping of *p*-orbitals. So, the compound is non-aromatic.

Cyclooctatetraene (Non-aromatic, non-planar)

■■
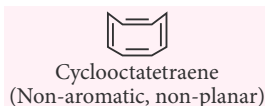
CROSSWORD

Readers can send their answer with complete address by 15th of every month to win exciting prizes.
*Winners' name with their valuable feedback will be published in next issue.*

ACROSS

1. Furnace used for annealing of gold. (6)

3. Mixture of CaS and Na_2CO_3. (8)

5. Process, by which white lead is prepared. (5)

6. An actinide element used in glass industry. (7)

9. Silicate having two units of SiO_4^{4-}. (12)

11. Element used in optophone. (8)

12. Lipids found in the membrane of brain and nerve cells. (12)

15. Oil of mirbane. (12)

16. The process by which muddy water can be purified. (11)

18. Roofing material. (4)

19. The region in an infrared spectrum below 1500 wavenumbers. (11)

20. A urinary antiseptic. (10)

22. Commercial name of toluene. (6)

23. 'Fight-or-flight' hormone. (10)

24. Acid present in coca-cola. (10)

25. Substances which form zwitter ions/internal salts. (10)

DOWN

2. A calcium compound, fluorescent in nature. (8)

3. Used in the manufacture of enamels and glazes for earthen pots. (5)

4. Class of drugs to which naproxen belongs. (10)

7. A neutral particle represented by symbol π^0. (5)
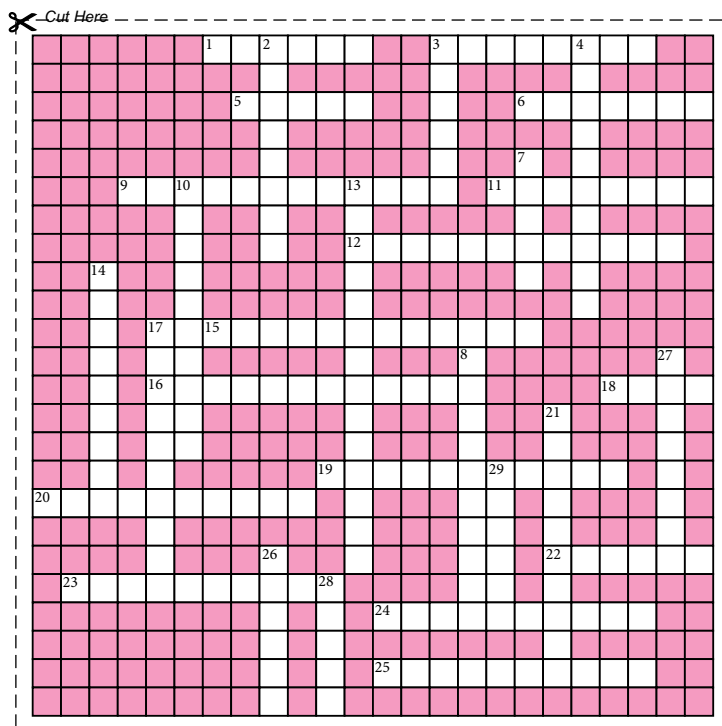
8. _____, also known as cyanoacrylate. (9)

10. The model, based on the results of scattering experiments was given by _____. (10)

13. Another name of [4] annulene. (14)

14. Reaction by which all aldehydes can be made to undergo Cannizzaro reaction. (9)

17. Mixture of ClO_2 and Cl_2 used as a bleaching agent. (10)

21. Reversible sol-gel transformation. (10)

26. A major constituent of Scots pine oil. (6)

27. Cyclic amides. (7)

28. Oxidation of toluene to benzaldehyde is _____ reaction. (5)

29. Units of viscosity. (5)